FORMATION OF HYDRATE FROM SINGLE-PHASE AQUEOUS SOLUTIONS

by

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ABSTRACT

FORMATION OF HYDRATE FROM SINGLE-PHASE AQUEOUS SOLUTIONS

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Experimental and theoretical research on the formation of hydrate from single-phase solutions of the hydrate former dissolved in water is described in this work. Two-phase equilibrium between carbon dioxide hydrate (H) and a water-rich liquid (L) are experimentally measured and theoretically described between 273 K and 280 K and at pressures to 60 MPa. Concentrations of carbon dioxide in the water phase ranging between 0.014 and 0.022 were studied. The theoretical and experimental results both indicate that the equilibrium pressure is very sensitive to concentration at all temperatures. These equilibria represent the solubility of carbon dioxide hydrate in a water phase and if a constant aqueous composition LH curve is extrapolated to the three-phase VLH curve, the composition characterizing the LH curve also represents the solubility of carbon dioxide in water at the VLH conditions. Since the solubility of carbon dioxide in water at hydrate- forming conditions is difficult to obtain, this method provides an excellent way of indirectly measuring this three-phase solubility.

DESCRIPTORS

Carbon dioxide solubility	Hydrate formation
Phase equilibrium	Single-phase solution

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1.0 INTRODUCTION

The potential impact of rising greenhouse gas levels in the atmosphere is a current global concern. Carbon sequestration offers the potential to reduce the buildup of CO_2 in the atmosphere and is a topic of ongoing research and debate (U. S. Department of Energy, 1999). Oceanic CO_2 sequestration has been proposed as a method of long-term sequestration of anthropogenic emissions of CO_2. Understanding the fate of CO_2 released into the deep ocean is therefore important to assessing the utility of this strategy for long-term sequestration. The environmental impact and economics are also important and are under investigation (U. S. Department of Energy, 1999).

Direct injection of CO_2 through pipes to ocean depths ranging from 1000 m to 3000 m is a leading candidate for introducing CO_2 into the deep ocean. However, formation of the ice-like CO_2 clathrate hydrate at the interface of CO_2 and seawater complicates the fate of liquid CO_2 injected into the ocean (Holder, et al., 1995). The physical and chemical behavior of CO_2 in the ocean needs to be understood, especially the impact of CO_2 hydrate on the injection and sequestration process.

Formation of CO_2 hydrate from a single-phase aqueous solution using only the hydrate former dissolved in the aqueous phase is the focus of this work. Generally, in the laboratory, hydrates are formed from two-phase systems consisting of a hydrate former in a separate gas (V) or liquid phase (L_2) and liquid water (L_1). Information in the literature addressing the formation of hydrate from a single-phase solution of hydrate former dissolved in water is limited (Holder, et al., 2001). Prior work done at the National Energy Technology Laboratory (NETL) has

demonstrated that if CO_2 hydrate forms from a two-phase system of either gaseous or liquid CO_2 and water, the hydrate formed was initially less dense than the aqueous solution. This is likely due to occluded bubbles or drops of CO_2 in the hydrate clusters. Such floating hydrate particles will diminish the effectiveness of ocean sequestration of CO_2. However, if CO_2 hydrate forms from a single-phase system, the hydrate formed was initially more dense than the aqueous phase. The formation of hydrates could enhance the ocean sequestration effort by causing the CO_2 to sink to even greater depths before it dissolves. (Holder, et al., 2001).

In this work, additional experimental single-phase CO_2 hydrate formation research was performed that compliments and extends previous work (Holder, et al., 2001) and further validates the thermodynamic model (Holder, et al., 1988) which describes the phase equilibrium of hydrate formation. Further modification and improvement to this model were also performed. Two-phase equilibrium between CO_2 hydrate (H) and a water-rich liquid (L_1) were experimentally measured and theoretically described between 273 K and 280 K and at pressures to 60 MPa.

2.0 LITERATURE REVIEW

2.1 CO_2 and carbon sequestration

Carbon dioxide levels in the atmosphere arising from the combustion of fossil fuel (gas, oil, and coal) and other human activities have increased substantially since the Industrial Revolution, and are expected to continue doing so. Although the long-term consequences of these changes are hotly debated, many scientists agree that rising atmospheric CO_2 concentrations could give a variety of serious environmental problems and CO_2 is quantitatively by far the greatest contributor (64%) to climate forcing among the gases arising from anthropogenic activity (Johnston, et al., 1999).

This problem has drawn attention throughout the world. In 1992, 167 nations signed the United Nations Framework Convention on Climate Change, which includes the objective to achieve " stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous interference with the climate system" (Johnston, et al., 1999).

Three approaches to manage carbon dioxide were proposed. One is to reduce the need for carbon source energy by improving energy efficiency. Another approach is to increase the use of low-carbon and carbon-free fuels and technologies. The third and newest approach-- carbon sequestration, which receives less attention to date than the other two approaches, is truly radical in a technology context. (U. S. Department of Energy, 1999)

Carbon sequestration is to capture and secure storage of carbon that would otherwise be emitted to or remain in the atmosphere. Six scientific/technological focus areas relevant to carbon sequestration were identified in order to achieve carbon emission reductions needed to mitigate the atmospheric CO_2 (U. S. Department of Energy, 1999):

1. Separation and Capture of CO_2
2. Ocean Sequestration
3. Carbon Sequestration in Terrestrial Ecosystems (Soils and Vegetation)
4. Sequestration of CO_2 in Geological Formations
5. Advanced Biological Processes for Sequestration
6. Advanced Chemical Approaches to Sequestration

Approximately 1 billion tones of carbon (GTC)/yr by 2025, and 4 GTC/yr by 2050 need to be sequestered in order to meet the goal adopted by Intergovernmental Panel on Climate Change (IPCC) of stabilizing the atmosphere at about 550 ppm CO_2. (Brewer, 2000) It is clear that advanced CO_2 sequestration is required. "Carbon Sequestration could be a major tool for reducing carbon emissions from fossil fuels. However, much work remains to be done to understand the science and engineering aspects and potential of carbon sequestration options." (U. S. Department of Energy, 1999)

2.2 Oceanic Sequestration of CO_2

The direct disposal of CO_2 to the deep oceans is one of the approaches that are receiving the greatest focus, as a means of ameliorating greenhouse gas induced climate change (Handa, 1990; Wong & Hirai, 1997; Ormerod, 1996; Ormerod & Angel, 1996). Specifically the proposals fall into three distinct categories: (Johnston, et al., 1999)

- Ocean fertilization, which fertilize open waters to increase primary production and hence to absorb more carbon in fixed form that will eventually be incorporated into the ocean sediments (Coale et al., 1996; Boyd et al., 2000; Markels, 2001)

- Disposal of captured CO_2 directly into oceans (Brewer, 2000)
- Injection of captured CO_2 into sub-seabed geological formations (Winter & Bergman, 1993)

The ocean represents a large potential sink for sequestration of anthropogenic CO_2 emissions. It is generally accepted that more than 80% of today's anthropogenic CO_2 emissions will eventually be absorbed naturally into the oceans, on a time scale of 1000 years. Ocean sequestration strategies attempt to investigate the possibility to speed up this process to reduce the peak of carbon dioxide concentration in the atmosphere and the rate of increase.

Technical approaches to introduce CO_2 into oceans include the following three methods (Johnston, et al., 1999):

- Introduction by pipeline into deep ocean by dissolution
- Dispersion following discharge of dry-ice blocks or liquid CO_2 from a ship
- Formation of a lake of liquid CO_2 in the deep sea

Most research effort has focused on the introduction of CO_2 by pipeline. The concept is illustrated in Figure 1 below:

If CO_2 is introduced into ocean at depths of less than 500m, carbon dioxide exists as a gas at ambient pressures and temperatures, and the bubble plumes created will rise in the seawater with most gas dissolving but some possibly escape to the atmosphere. Optimistically, the retention time of the gas would be relatively short (about 50 years). At depth between 500m and 3000m, carbon dioxide exists as a positively buoyant liquid. It will form a droplet which will probably be which are solid, negatively buoyant, ice-like compounds (Adams et al., 1995). "Retention times

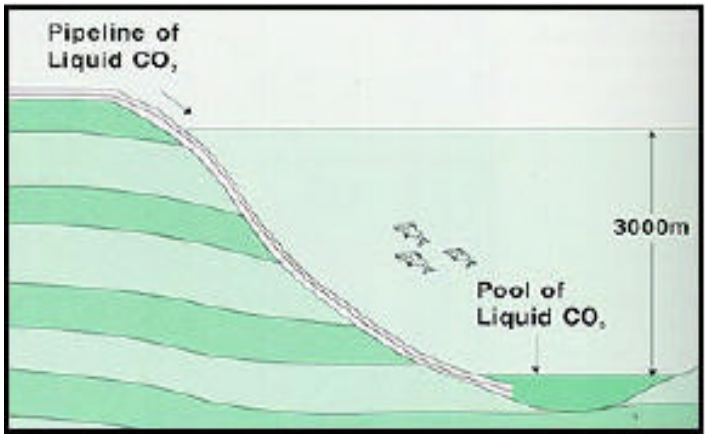

Figure 1 Concept for introducing CO_2 captured from power and industrial plant into deep ocean by land based pipelines.

in these cases should be much greater since deep water exchanges with surface water at a much lower rate than surface water interacts with the atmosphere in the upper mixed layer of the sea." (Johnston, et al., 1999) In general, the retention time for disposal of CO_2 into the ocean is considered as a function of the depth where it is discharged (Wong & Matear, 1993). There are considerable variations and uncertainty in likely residence times because the models (Bacastow et al., 1993; Ormerod, 1996) used to predict these times depend upon the data used to tune them and upon the accuracy of constant factors describing physical and chemical phenomena. An accurate description of the fate of CO_2 injected into ocean water is necessary for predicting the behavior of large-scale ocean disposal schemes. The first successful field experiment where CO_2 hydrate was formed in the deep ocean was performed by Monterey Bay Aquarium Research Institute (Brewer et al., 1999). Associated costs of oceanic disposal of CO_2 in terms of energy and economic penalties and impacts on the marine environment also need careful investigation and full understanding.

2.3 Nature of Hydrates

Gas hydrates are non-stoichiometric, crystalline molecular complexes formed from water and low molecular weight gases. The water molecules form a lattice structure and the gas molecules occupy the interstitial vacancies of the lattice. There is no chemical association between gas and water molecules. The gas molecules interact with the water molecules through van der Waals type dispersion force. Instead, the water molecules that form the lattice are strongly hydrogen bonded with each other (Holder, et. al., 1988; van der Waals, et. al., 1959; Parrish & Prausnitz, 1972). Although hydrates were first discovered by Davy in 1810, gas hydrates became a subject of investigation after it was been found out that formation of gas hydrates was responsible for the plugging of natural gas process and transportation lines (Hammerschmidt, 1934).

All common natural gas hydrates belong to the three crystal structures: cubic I (sI), cubic structure II (sII), and hexagonal structure (sH). Structure I is formed with gas molecules smaller than 6 $\mathring{A}$, such as methane, ethane, carbon dioxide and hydrogen sulfide. Structure II is formed with gas molecules somewhat lager (6 $\mathring{A}$ < d < 7 $\mathring{A}$), such as propane or iso-butane. Still larger molecules (7 $\mathring{A}$ < d < 9 $\mathring{A}$), such as iso-pentane or neo-hexane can form structure H when accompanied by smaller molecules such as methane, hydrogen sulfide or nitrogen. Structure I and II are shown in Figure 2 (Sloan, 1998).

At high pressure and low temperature, CO_2 and water can form structure I hydrate. The unit cell of the structure I hydrate contains eight cavities, two small and six large, which are constructed from 46 water molecules. Each cavity can at most hold one CO_2 molecule. Research in CO_2 hydrates formation has been performed in the laboratory at the temperature range from

151.5 K to 292.7 K and the pressure range from 5.35 kPa to 186.2 kPa (Miller & Smythe, 1970; Takenouchi & Kennedy, 1965; Sloan, 1998).

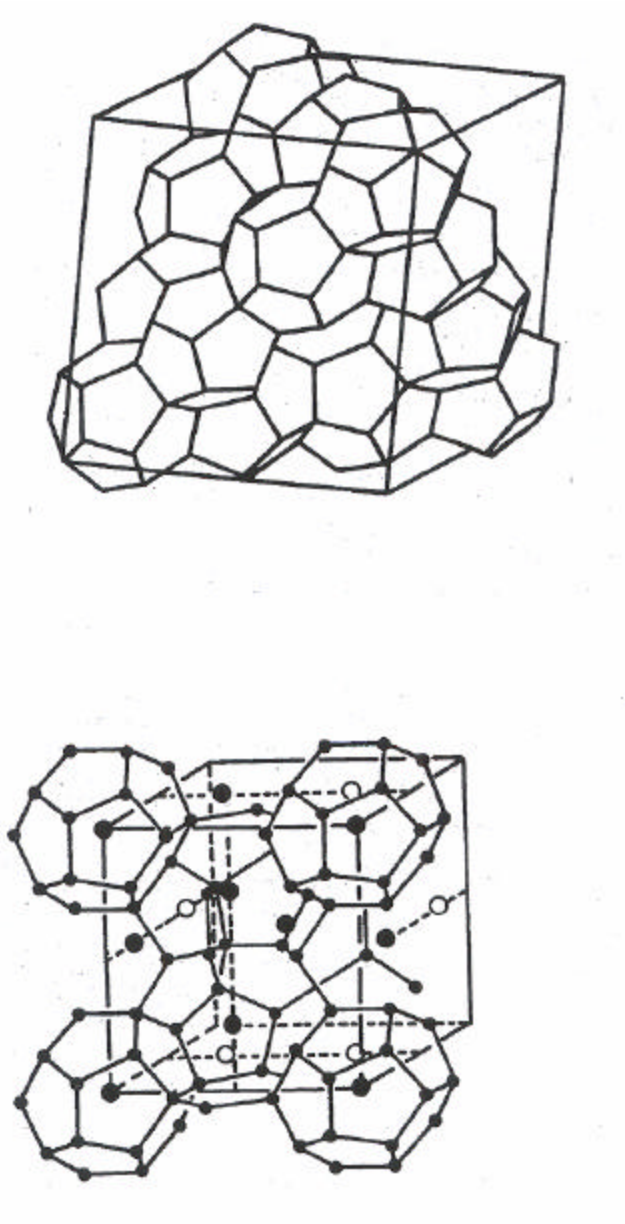

Figure 2 Gas Hydrate Structure I and Structure II

2.4 Formation of CO_2 Hydrate

A considerable amount of research and experimental data in formation of CO_2 hydrate from two-phase system consisting of CO_2 in a separate gas (V) or liquid phase (L_2) and liquid water (L_1) have been published (von Stackelberg & Muller, Unruh & Katz, 1949; Takenouchi & Kennedy, 1946; Robinson & Mehta, 1971; Berecz & Balla-Achs, 1983; Ng & Robinson, 1985). Several research results indicate that hydrates formed from two-phase system are initially less dense than water and float. Such floating hydrate particles will diminish the effectiveness of ocean sequestration of CO_2. Research in formation of hydrate from single-phase is limited in literature. However, the previous research performed at the NETL has demonstrated that if CO_2 hydrate forms from a single-phase system, the hydrate formed was initially more dense than the aqueous phase (Holder, et al., 2001; Warzinski, et al., 2000; Warzinski, et al, 1995). This may have application to carbon sequestration.

3.0 DESCRIPTION OF EXPERIMENT

The experimental observations were made in a high-pressure, variable-volume viewcell (HVVC) of about 10 cm^3 to 40 cm^3 capacity. A sapphire window permits visual observation of the contents of the HVVC. A small oval-shaped high-density Teflon coated magnetic stirring bar was used to promote mixing within the HVVC. The entire system was enclosed in a temperature programmable environmental chamber that could maintain the temperature of interest to within 0.1 K. Water purified by reverse osmosis and deionization (18 mega ohm-cm) and CO_2 (SFC grade, 99.99+% purity) were used in the experiments reported here. Platinum Resistance Temperature Detector (RTD) used in the experiments has an accuracy of ± 0.2% of reading. Pressure of the viewcell was measured by Heise ATS2000 Digital Pressure Transducer with an accuracy of ± 0.02% of span. Ethylene Propylene Diene Monomer (EPDM) O-ring was used to provide the sealing of the cell.

The HVVC was filled with water injected into the HVVC with a syringe pump. The amount of liquid CO_2 injected through another syringe pump was determined from the volume delivered by using the density for CO_2 obtained from the IUPAC International Thermodynamic Tables of the fluid state for carbon dioxide at the pressure and the temperature of the laboratory. After dissolution of the added CO_2, the system was quickly subcooled to 271 K, and then heated up to 290 K at the rate of 0.3 K/hr. Overview of the laboratory setup and schematic of equipment are shown in Figure 3 and Figure 4, respectively.

Figure 3 Overview of Laboratory Setup

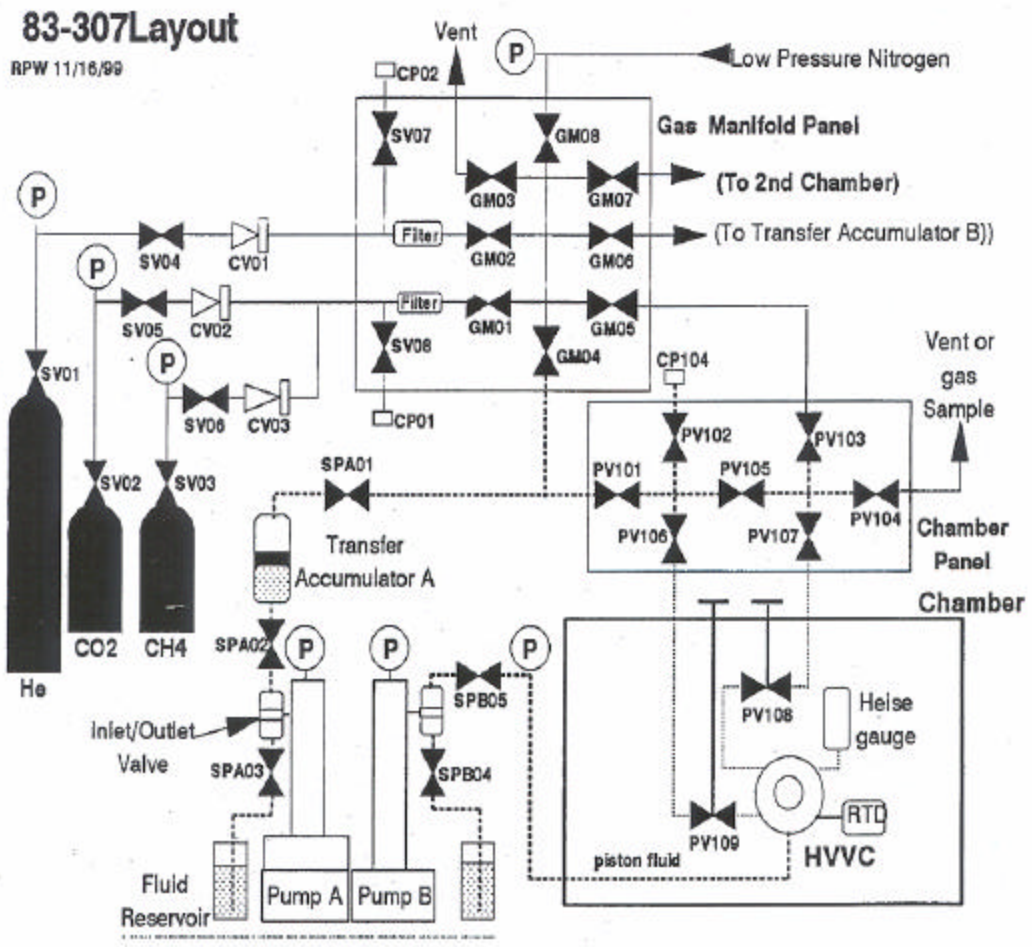

Figure 4 Schematic of Equipment

4.0 RESULTS AND DISCUSSION

4.1Analysis of the Experimental Results

Five sets of experiments were performed in which CO_2 hydrate was formed from single-phase aqueous solutions. Mole fractions of CO_2 from 0.0160 to 0.020 were studied with accuracy of ± 2%. The pressure versus temperature trace for a typical cycle is presented in the Figure 5. Note that this trace is not consistent with the formation of ice. Ice was not observed in these experiments.

Because of metastability in hydrate formation, the hydrate dissociation trace obtained during heating was used to evaluate the equilibrium point. Due to the difficulty in qualifying the equilibrium point from the pressure vs. temperature trace, the slope of dissociation curve vs. temperature was determined as shown in Figure 6. The peak of this curve represents the point of maximum dissociation, but does not represent the equilibrium for the overall CO_2 concentration, because the water phase composition is changed due to removal of CO_2 into the hydrate phase. The minimum in this trace indicates the absence of any further hydrate dissociation and represents a temperature slightly above the equilibrium value. The equilibrium is taken as the midpoint between the peak and the minimum. This produces an estimated uncertainty (±0.5K). Visual observation confirms the selection of this point. The equilibrium point is indicated in the Figure 6. Experiments are continuing at NETL to reduce the uncertainty of this point.

From the experiments, we found out that mixing was a very important factor in obtaining accurate equilibrium data, and the stirring bar played a key role. Different shapes and materials of the stirring bar were tested and it turned out that oval-shaped high-density Teflon coated magnetic stirring bar gave the best performance. We also found out that cooling rate had no

effect on equilibrium and 0.3K/hr of heating rate was satisfactory to obtain accurate equilibrium data.

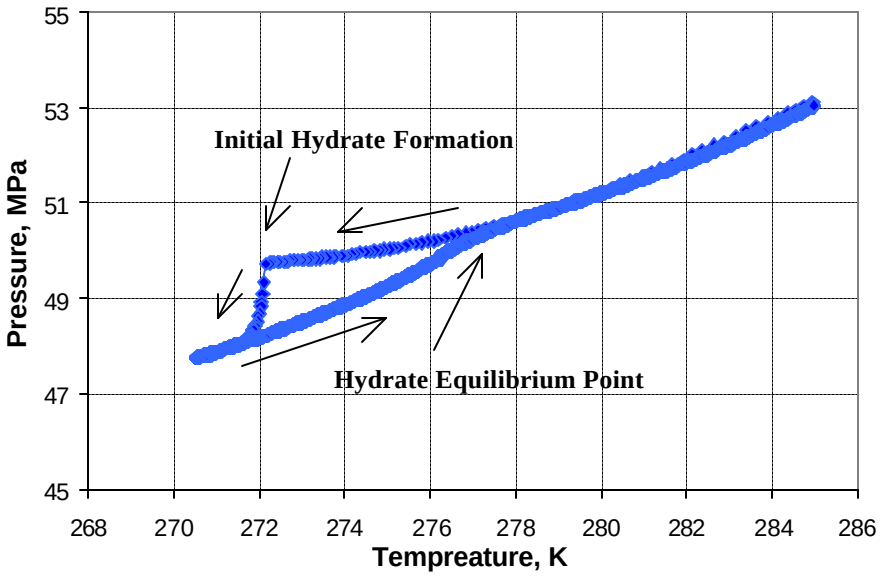

Figure 5 Pressure vs. Temperature history of an experiment in which hydrates were formed and decomposed in a single-phase solution of dissolved CO_2 in water. The trace was preceded as indicated in light arrows.

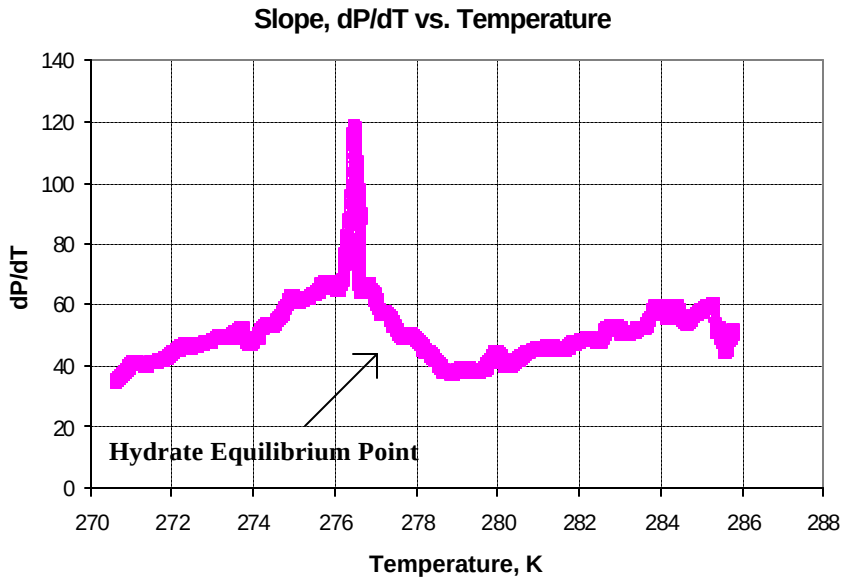

Figure 6 dP/dT vs. Temperature for dissociation of CO_2 hydrate in a single-phase solution

4.2 Thermodynamic Models for Hydrate Equilibrium

The basic model for hydrate equilibrium used by author is based on the work of van der Waals and Platteeuw(vdWP) (1959) and extended by Parrish and Prausnitz (1972) by using the Kihara potential with modified Kihara parameters. This method was substantially simplified by John and Holder (1981). Bazant and Trout (2001) applied an analytical "inversion" method based on the standard statistical model of vdWP to extract cell potentials directly from experimental data. In this work, the John and Holder model was modified to allow its application to our experimental data.

For the water species in the hydrate phase, the value of $\Delta\mu_H$ (the chemical potential of water in the hydrate phase) is obtained by using the following equation (Holder, et al., 1988):

$$\Delta m_H = -RT \sum_{j,cavities} n_j \ln\left(1 - \sum_i q_{ji}\right) \qquad (1)$$

Where, ν_j is the ratio of j-type cavities present to the number of water molecules present in the hydrate phase and

$$q_{ji} = \frac{C_{ji} f_i}{1 + \sum_i C_{ji} f_i} \qquad (2)$$

Where, C_{ji} is the Langmuir constant for species i in cavity j; f_i is the fugacity for the hydrate forming species; θ_{ji} is the fraction of j-type cavities, which are occupied by i-type gas molecules. The value of $\Delta\mu_L$ (the chemical potential difference of water in the water-rich phase) is calculated from the following equation (Holder, et al., 1980):

$$\frac{\Delta m_L}{RT} = \frac{\Delta m^0}{RT_o} - \int_{T_o}^{T_F} \frac{\Delta h}{RT^2} dT + \int_0^P \frac{\Delta V}{RT} dP - \ln x_w \quad (3)$$

The terms Δh and ΔV are the molar enthalpy and volume differences, respectively, between the empty hydrate or liquid water phases.

At equilibrium, $\Delta\mu_H = \Delta\mu_L$, hydrates can exist.

For the present work, the above models were simplified by omitting the last term in Equation (3), because the concentration of water (x_w) is very close to unity in water-rich solutions. The first two terms on the right represent $\Delta m_L(T, P = 0)$, the chemical potential difference at a fixed temperature and zero pressure. At a fixed temperature, hydrate forms from single-phase solution. The following relationship is obtained:

$$-\sum_{j,cavities} n_j \ln\left(1 - \sum_i q_{ji}\right) = \frac{\Delta m_L}{RT}(T, P = 0) + \int_0^P \frac{\Delta V}{RT} dP \quad (4)$$

When hydrate forms from two-phase solution, the following relation is obtained:

$$-\sum_{j,cavities} n_j \ln\left(1 - \sum_i q_{ji}^{VLH}\right) = \frac{\Delta m_L}{RT}(T, P = 0) + \int_0^{P^{VLH}} \frac{\Delta V}{RT} dP \quad (5)$$

Subtracting equation (5) from equation (4), following equation is obtained:

$$-\sum_{j,cavities} n_j \ln\left(\frac{1 - \sum_i q_{ji}}{1 - \sum_i q_{ji}^{VLH}}\right) = \int_{P^{VLH}}^P \frac{\Delta V}{RT} dP \quad (6)$$

Since for single hydrate species,

$$\frac{1 - q_{ji}}{1 - q_{ji}^{VLH}} = \frac{1 + C_{ji} f_{ji}^{VLH}}{1 + C_{ji} f_i}$$

The following equation is obtained:

$$\sum_j n_j \ln\left[\frac{\frac{1}{C_{ji} f_i^{VLH}} + \frac{f_i^{sat}}{f_i^{VLH}} \exp\left(\frac{\bar{V}_i (P - P^{sat})}{RT}\right)}{\frac{1}{C_{ji} f_i^{VLH}} + 1}\right] = \frac{\Delta V (P - P^{VLH})}{RT} \qquad (7)$$

Where, P^{sat} and f^{sat} are the pressure and corresponding fugacity of the CO_2, which are required to dissolve the experimental levels of CO_2 in the water phase of the given temperature. We use the experimental solubility of CO_2 in water (Kirk-Othmer, 1993) to obtain these values. The exponential term is the Poynting correction (J. M. Prausnitz, 1969) to f^{sat}, giving the fugacity at pressure P. $\bar{V}_i$ is the partial molar volume of CO_2 in liquid water.

Equation (7) can be solved for the pressure. In this approach, reference state properties are not relevant, and the values of the pressures can be easily compared to those obtained in our experiments. Further simplification was also applied as following:

In some case, $C_{ji} > 9$, $C_{ji} f_i >> 1$. $\frac{f_i^{sat}}{f_i^{VLH}} \approx \frac{P^{sat}}{P^{VLH}}$

Then, the following equation is obtained:

$$\sum_j n_j \ln\left[\frac{P^{sat}}{P^{VLH}} \exp\left(\frac{\bar{V}_i (P - P^{sat})}{RT}\right)\right] = \frac{\Delta V (P - P^{VLH})}{RT} \qquad (8)$$

In this equation, P is the equilibrium pressure for hydrates formed from single-phase solutions. The values of all the other variables can be obtained from either experiments or literature data. Figure 7 presents the comparison of experimental and predicted data that are calculated by equation (7) and (8).

The vertical dash line represents T=273.15 K region. The lines for the calculated results obtained by equation (7) are compared to the dash lines obtained by equation (8).

More information can be obtained from Figure 3 as shown in Figure 8 and 9.

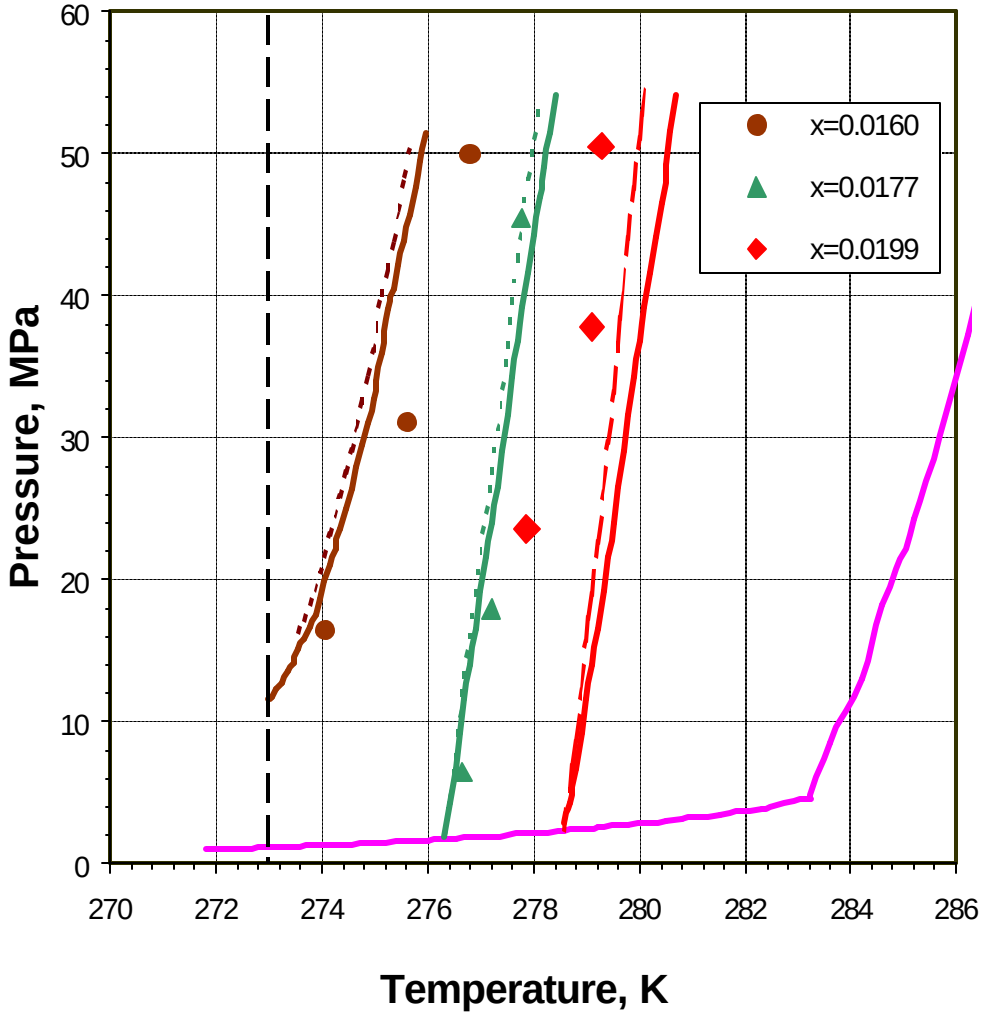

Figure 7 Comparison of Experimental and Predicted data by using modified models

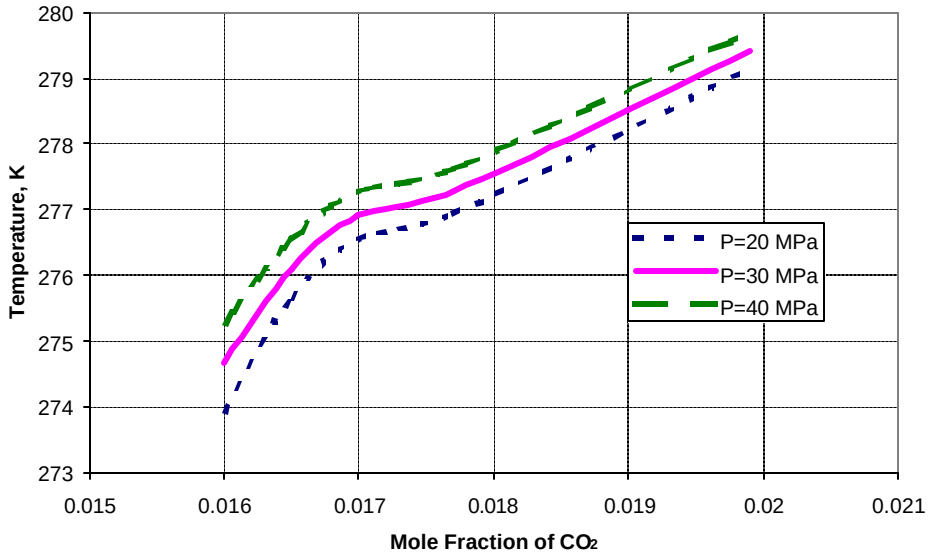

Figure 8 Hydrate equilibrium temperature vs. Mole fraction of CO_2 at constant pressure

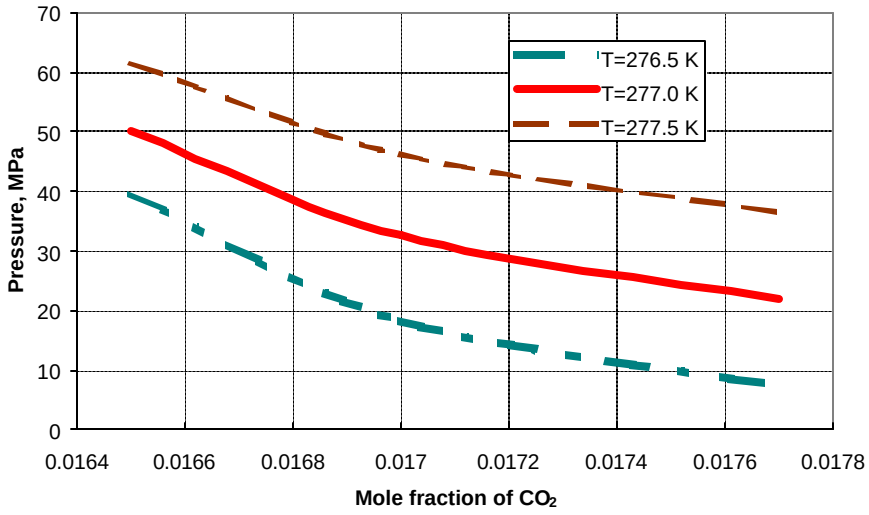

Figure 9 Pressure vs. Mole fraction of CO_2 at constant Temperature

From Figure 8 and 9, it is very clear that for a given CO_2 concentration, the higher the pressure that the system can have, the higher the temperature hydrate can form at. For a given

temperature, the higher the concentration of CO_2, the lower pressure will be required in order to form hydrate.

Comparison of experimental data and calculated results by simplified and exact models is shown below. X is mole fraction of CO_2; Texp is the experimental temperature; Tsim is the calculated temperature calculated by simplified model; Texa is the calculated temperature calculated by exact model.

Table 1 Comparison of experimental data and calculated results by simplified and exact models

X	P (MPa)	Texp (K)	Tsim (K)	Texa (K)
0.0199	50.58	279.3	280.0	280.6
	37.87	279.1	279.6	280.1
	23.58	277.9	279.2	279.6
0.0177	45.26	277.8	277.8	278.0
	18.00	277.2	277.1	277.1
	6.65	276.5	276.6	276.6
0.0160	50.01	276.8	275.7	275.8
	31.14	275.6	274.6	274.7
	16.47	274.0	273.6	273.7

5.0 SUMMARY AND CONCLUSIONS

Formation of CO_2 hydrate from single-phase aqueous solutions was performed in this work. The modified and simplified theoretical models can give reasonable prediction of the conditions of hydrate formation equilibria from single-phase aqueous solutions, and will have potential usage in ocean sequestration of CO_2. Further investigation of phase equilibrium condition is needed to have better understanding of these phenomena. In addition, the approximations made in the model should be examined and a more rigorous approach taken.

APPENDIX

```
C       ******************************************************
C
C       CALCULATION OF HYDRATE PHASE EQUILIBRIA.
C       ******************************************************
C       THIS PROGRAM CALCULATES PCALC WHEN TENURED PEXP.
C       LANGMUIR COEFFICIENTS ARE CALCULATED BY USING
C       Q* CORRELATION METHOD.
C
C
C       25 GASES ARE INCORPORATED INTO THE PROGRAM.
C       MIXTURES OF UP TO 10 COMPONENTS CAN BE STUDIED.
C
C       ********    COMMON STATEMENTS     ********
C
        PROGRAM HYD
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        IMPLICIT INTEGER (I-N)
        CHARACTER*5 YCOMP,YNAME,YNAMEL,YNAMEIM
        CHARACTER*4 AQ
        DIMENSION YNAME(25)
        DIMENSION YCOMP(10)
        DIMENSION ICASE(30),ILEN(31)
        DIMENSION A(10),SIGMA(10),EPS(10),AMW(10),TC(10),VC(10),PC(10)
        DIMENSION ZAA(1,25),AK(25,25)
        DIMENSION IISCO(25),PPEXP(100)
        DIMENSION KYP(20),NCODE(25)
        DIMENSION OMEGA(10),ESTAR(10),C1RKV(10),C2RKV(10),C1RKL(10)
        DIMENSION C3FREF(10),C4FREF(10),C1FREF(10),C2RKL(10)
        DIMENSION C2FREF(10),C0FREF(10)
        DIMENSION XX(13),KK(25),ZA(20),ICODE(10)
        DIMENSION YNAMEIM(10)
        DIMENSION YNAMEL(10)
        COMMON/BKSB/NPT,NSETS,IFLAG
        COMMON/BLOCK/ISOLVE
        COMMON/AZ/KK,N,MK
        COMMON/NC/NCODE,NCOMP
        COMMON/DV/PVAP(100),AA(3),AB(3),PSAT(3,100),XY(100)
        COMMON /AMOL/MA,ISCODE(10)
        COMMON/TEXPT/PEXP(100),X(15,100),IS(100),T(100),YEXP(100)
        COMMON/SERDAT/T1(100),DT(100),T2(100)
        COMMON/FUND/SIGMA,EPS,A
        COMMON/XXX/XX,DH
        COMMON/COR/EPSH,DDU,DDH,BETA1,GAMMA
        COMMON/VDO/SIGH1,SIGH2
        COMMON/BKSA/AK
        COMMON/BKSC/IWATER,IPOS,ISTR,IDH
        COMMON/PHAS/NVLLH
        COMMON/STRUC/NSTRUC
        COMMON/IMP/IMPURE,IMCODE,XIMP(100),YCO2(100)
        COMMON/SOLUT/XSOLU,ACTIV,YYYCO2
        COMMON/SEQ/ISEQ,TMIN,DELT,TMAX,TQL
        COMMON/LIQUID/LIQ
C       ****************************************
C
C
C       ****  READ IN EACH COMPONENT  ****
C
```

```
      DATA YNAME/'CH4','C2H6','C2H4','C3H8','C-C3',
     *'N-C4','I-C4','C-C4','C5H12','I-C5','NE-C5','C-C5',
     *'H20','H2','CO2','O2','N2','H2S','XE','AR','KR',
     *'SF6','CIC4','TRC4','NONE'/
      DATA YCOMP / 'Y-1','Y-2','Y-3','Y-4','Y-5','Y-6','Y-7',
     *'Y-8','Y-9','Y-10'/
      DATA YNAMEL/'XL1','XL2','XL3','XL4','XL5','XL6','XL7',
     *'XL8','XL9','X10'/
      DATA YNAMEIM / 'MEOH','ETOH','PROH','NACL','CACL2','KCL'
     * ,'NH3','ETGLY','DEGLY','TRGLY'/
C
C
C
C
C
C
C
C
C     COMPONENT IDENTIFIERS,WHERE FOLLOWING CODE APPLIES.
C
C
C            **** 1= METHANE
C            **** 2= ETHANE
C            **** 3= ETHYLENE
C            **** 4= PROPANE
C            **** 5=CYCLO-PROPANE
C            **** 6= N-BUTANE
C            **** 7= ISO-BUTANE
C            **** 8= CYCLO-BUTANE
C            **** 9= PENTANE
C            **** 10= ISO-PENTANE
C            **** 11= NEO-PENTANE
C            **** 12= CYCLO-PENTANE
C            **** 13= WATER
C            **** 14= HYDROGEN
C            **** 15= CARBON-DI-OXIDE
C            **** 16= OXYGEN
C            **** 17= NITROGEN
C            **** 18= HYDROGEN SULFIDE
C            **** 19= XENON
C            **** 20= ARGON
C            **** 21= KRYPTON
C            **** 22= SULFUR HEXAFLOURIDE
C            **** 23= CIS-2-BUTENE
C            **** 24= TRANS-2-BUTENE
C            **** 25= NO COMPONENT PRESENT
C
C
C
C       IMPURITY IDENTIFIERS, WHERE THE FOLLOWING CODE APPLIES
C
C          ** 1=METHANOL
C          ** 2=ETHANOL
C          ** 3=PROPANOL
C          ** 4=SODIUM CHLORIDE
C          ** 5=CALCIUM CHLORIDE
C          ** 6=POTTASIUM CHLORIDE
```

```
C             ** 7=AMMONIA
C             ** 8=ETHYLENE GLYCOL
C             ** 9=DIETHYLENE GLYCOL
C             ** 10=TRIETHYLENE GLYCOL
C
C
C
C
C       FOLLOWING DATA IS READ FROM FILE FOR12.DAT:
C       1>ISOLVE=SELECT EQ. OF STATE: 1=PENG ROB. 2=RED. KWONG
C       2>ISTR=PRINT STRUCTURE DATA: 1=YES, 2=NO
C       3>ILANG=PRINT LANGMUIR CONSTS.: 1=YES, 2=NO
C       4>IN=PRINT SWITCH: 1=PRINT COMP. LIST 2=NO COMP LIST
C       5>NSETS=NUMBER OF ON LINE DATA SETS TO RUN
C              =0 IF USES ENTERS HIS OWN EXPT. OR GUESSED DATA
C       6>IWATER= SWITCH FOR WATER CONTENT CALC FOR 2 & 3 PHASE SYS
C               = 0 : DONT PERFORM CALCULATIONS
C               = 1 : CALCULATE YH2O  GIVEN P
C               = 2 : CALCULATE YH2O AND COMPARE WITH EXPMTL DATA
C       7>IPOS=COMPONENT POSITION OF WATER I.E. 1,2,0R 3 ...
C      8>NVLLH=SWITCH FOR QUADRUPLE POINT CALCULATION
C             =0 :DONT PERFORM QUAD POINT CALCULATIONS
C             =1 :CALCULATE QUADRUPLE POINT. IF NVLLH IS 1 THEN
C                         NSTRUC SHOULD NOT BE ZERO.
C      9>NSTRUC=SWITCH FOR CHECKING THE PRESENCE OF 'V L H1 H2' QUAD POINTS
C              =1 :ONLY ONE HYDRATE STRUCTURE IS FORMED AND IS THE ONE
C                         GIVEN IN DATA.
C              =2 :CHECK FOR 'V L H1 H2' QUAD POINTS
C     10>IMPURE=SWITCH FOR CALCULATIONS IN THE PRESENCE IMPURITIES
C              =0 :NO IMPURITIES IN WATER
C              =1 :IMPURITIES ARE PRESENT (SEE IMPURITY CODES)
C     11>ISEQ=SWITCH FOR CALCULATING EQUILIBRIUM CURVE BETWEEN TEMPERATURES
C                  T1(I) AND T2(I) AT INTERVALS OF DT(I)
C            =0 :NO SEQUENTIAL CALCULATIONS
C            =1 :SEQUENTIAL CALCULATIONS UPTO TEMPERATURE T2(I)
C            =2 :SEQUENTIAL CALCULATIONS UPTO THE QUADRUPLE POINT(VLLH)
C     12>LIQ=SWITCH FOR CALCULATING  L1 L2 H EQUILIBRIA ONLY
C              =0 :GAS COMPOSITION IS GIVEN
C              =1 :LIQUID COMPOSITION IS GIVEN
C       13>IDH=SWITCH FOR CALCULATING HEAT OF DISSOCIATION
C             =0 NO CALCULATIONS PERFORMED
C             =1 HEAT OF DISSOCIATION IS CALCULATED
C
C       14>MA=NUMBER OF COMPONENTS
C       15>KK(I)=CODE OF EACH COMPONENT
C       16>N=NUMBER OF DATA POINTS
C       17>EXPERIMENTAL HYDRATE CONDITIONS SUCH AS
C       P/PSIA,T/DEG.R,Y(I),I=1,MA
C
C
C       * * READ IN OPTION SWITCHES * *
C
      OPEN(12,FILE='TAPE12.DAT',STATUS='OLD')
        OPEN(06,FILE='HYDOUT.DAT',STATUS='UNKNOWN')
        READ(12,104)AQ
        READ(12,200)ISOLVE,ISTR,ILANG,IN
        GO TO(90,91),IN
```

```
  90    CONTINUE
        WRITE(06,301)
  91    CONTINUE
C
C       * * READ IN NUM OF ON LINE SETS TO RUN AND WATER SWITCH * *
C
        READ(12,104)AQ
        READ(12,302)NSETS,IWATER,NVLLH,NSTRUC,IMPURE,ISEQ,LIQ,IDH
        IF(NVLLH.EQ.1.AND.NSTRUC.EQ.0)GO TO 1002
        IF(IWATER.NE.0.AND.NVLLH.EQ.1)GO TO 1003
        IF(ISEQ.EQ.2.AND.NVLLH.EQ.0)GO TO 1004
        IF(LIQ.EQ.1.AND.ISEQ.EQ.1.AND.NVLLH.EQ.1)GO TO 1005
        IF(LIQ.EQ.1.AND.ISEQ.EQ.2)GO TO 1006
        IFLAG=1
C
C       * * SET CONDITIONS FOR USER'S EXPT OR GUESSED DATA * *
C
        IF(NSETS.NE.0)GO TO 56
        ILEN(1)=0
        ICASE(1)=1
        IFLAG=0
C
        NSETS=1
        GO TO 57
C
  56    READ(12,104)AQ
C
C       * * READ IN CODES FOR ON LINE DATA SETS TO BE RUN * *
C
        DO 51 I=1,NSETS
        READ(12,202)ICASE(I)
  51    CONTINUE
        READ(12,104)AQ
C
        ILEN(1)=0
C
C       * * READ IN TOTAL NUMBER OF ON LINE DATA SETS * *
C       * * PRESENT IN FOR12.DAT
C
        READ(12,202)NTSETS
        READ(12,104)AQ
        NTSETS=NTSETS+1
C
C       * * READ IN LENGTH OF EACH DATA ON LINE DATA SET * *
C
        DO 50 I=2,NTSETS
        READ(12,202)ILEN(I)
  50    CONTINUE
        READ(12,104)AQ
C
C       * * CONVERT ILEN VALUES TO CUMULATIVE VALUES * *
C
        DO 55 I=2,NTSETS
        ILEN(I)=ILEN(I)+ILEN(I-1)
  55    CONTINUE
C
C
```

```
  57    IMOVE=ILEN(ICASE(1))
C
C       * * MOVE THROUGH FOR12.DAT AND GET DESIRED DATA * *
C
        DO 983 IJK=1,NSETS
        IF(IMOVE.EQ.0)GO TO 54
        IF(IJK.EQ.1)GO TO 65
        IMOVE=ILEN(ICASE(IJK))-ILEN(ICASE(IJK-1)+1)
        IF(IMOVE.EQ.0)GO TO 54
C
  65    DO 53 I=1,IMOVE
        READ(12,104)AQ
 104    FORMAT(A4)
  53    CONTINUE
  54    IMOVE=1000
C
C
        READ(12,202) MA
C
C   ** CHECK WHETHER IMPURITY CALCULATION IS REQUIRED **
        IF(IMPURE.EQ.1)GO TO 185
        READ(12,308) (KK(I),I=1,MA)
        GO TO 186
 185    READ(12,309)(KK(I),I=1,MA),IMCODE
C
C   ** CHECK FOR PRESENCE OF CO2 WITH INHIBITOR **
C
        DO 1060 JJ=1,MA
        IF(KK(JJ).EQ.15)JJ1=JJ
 1060   CONTINUE
C       *********    READ IN NUMBER OF DATA POINTS   **********
C
 186    READ(12,305) N
        NPT=N
C
C       CHECK FOR HEAT OF DISSOCIATION CALCULATIONS
C
        IF(IDH.EQ.0) GO TO 327
        IF(ISEQ.EQ.1) GO TO 378
        IF(IMPURE.EQ.1) GO TO 326
        DO 328 I=1,N
        READ(12,329) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA)
 328    CONTINUE
        GO TO 12
  378    CONTINUE
        IF(IMPURE.EQ.0) GO TO 675
        DO 468 I=1,N
        READ(12,969) PEXP(I),T1(I),DT(I),T2(I),IS(I),(X(J,I),J=1,MA),
     1  XIMP(I)
 468    CONTINUE
        GO TO 12
 675    CONTINUE
        DO 8132 I=1,N
        READ(12,968) PEXP(I),T1(I),DT(I),T2(I),IS(I),(X(J,I),J=1,MA)
 8132   CONTINUE
        GO TO 12
 326    CONTINUE
```

```
        DO 341 I=1,N
        READ(12,330) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA),XIMP(I)
 341    CONTINUE
        GO TO 12
 327    CONTINUE
C       CHECK FOR WATER CALCULATION
        IF(IWATER.EQ.0.OR.IWATER.EQ.1)GO TO 67
C
C       **********    READ IN N DATA POINTS     **********
        DO 123 I=1,N
        READ(12,100) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA),YEXP(I)
 123    CONTINUE
        GO TO 12
 67     IF(IMPURE.EQ.0)GO TO 567
C       **CHECK WHETHER SEQENTIAL CALCULATION WITH IMPURITIES IS REQUIRED
C
C
        IF(IMPURE.EQ.1.AND.ISEQ.EQ.0)GO TO 569
        DO 221 I=1,N
        READ(12,181) PEXP(I),T1(I),DT(I),T2(I),IS(I),(X(J,I),J=1,MA)
     1,XIMP(I)
C
C    ** CHECK FOR PRESENCE OF CO2 WITH IMPURITY **
C
        YCO2(I)=X(JJ1,I)
 221    CONTINUE
        GO TO 12
 569    DO 222 I=1,N
        READ(12,111) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA),XIMP(I)
        YCO2(I)=X(JJ1,I)
 222    CONTINUE
        GO TO 12
C   ** CHECK WHETHER SEQUENTIAL CALCULATION IS REQUIRED **
 567    IF(ISEQ.EQ.0)GO TO 568
        DO 240 I=1,N
        READ(12,180) PEXP(I),T1(I),DT(I),T2(I),IS(I),(X(J,I),J=1,MA)
 240    CONTINUE
        GO TO 12
 568    DO 122 I=1,N
        READ(12,100) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA)
 122    CONTINUE
C
C
 12     CONTINUE
C
C
C       ********    WRITE OUT ALL INPUT DATA    ***********
        DO 978 I=1,MA
C
        WRITE(06,310) I,YNAME(KK(I))
 978    CONTINUE
        IF(IMPURE.EQ.1)WRITE(6,344)YNAMEIM(IMCODE)
        IF(IFLAG.NE.0)GO TO 58
        WRITE(06,105)(YCOMP(I),I=1,MA)
        GO TO 59
  58    IF(LIQ.EQ.0)WRITE(06,101)(YCOMP(I),I=1,MA)
        IF(LIQ.EQ.1)WRITE(06,101)(YNAMEL(I),I=1,MA)
```

```
  59    WRITE(06,103)
        IF(IMPURE.EQ.0)GO TO 182
        DO 95 I=1,N
        IF(ISEQ.EQ.1.OR.ISEQ.EQ.2)T(I)=T1(I)
        WRITE(6,112) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA),XIMP(I)
 95     CONTINUE
        GO TO 97
 182    DO 94 I=1,N
        IF(ISEQ.EQ.1.OR.ISEQ.EQ.2)T(I)=T1(I)
        WRITE(6,102) PEXP(I),T(I),IS(I),(X(J,I),J=1,MA)
 94     CONTINUE
 97     WRITE(6,315)
C
C       CALL FUN TO EVALUATE PCALC AS A FUNCTION
C       OF TEMPERATURE AND MOLE FRACTION.
C
C
        CALL FUN(NN,XX,FF)
        XX(1)=SIGH1
        XX(2)=SIGH2
        XX(3)=EPSH
        XX(4)=DDU
        XX(5)=DDH
        XX(6)=BETTA1
        XX(7)=GAMMA
        IF(ILANG.NE.1)GO TO 983
        WRITE(06,812) XX(1),XX(3),XX(4),XX(5),XX(6),XX(7),XX(2)
C
C
 983    CONTINUE
C
C
C
C
C
C
C       *******    THE FOLLOWING ARE FORMAT STATEMENTS ONLY  *******
 309    FORMAT(1(/),11(I2,1X))
 968    FORMAT(4(F5.0,1X),I1,1X,9(F5.0,1X))
 969    FORMAT(4(F5.0,1X),I1,1X,9(F5.0,1X))
 344    FORMAT(' IMPURITY',A15,'  PRESENT IN WATER')
 112    FORMAT(3X,2(F10.3,4X),4X,I1,6X,11(F6.4,2X))
 853    FORMAT(' ERROR IN INPUT DATA ISEQ=2 AND LIQ=1')
 843    FORMAT(' ERROR IN INPUT DATA LIQ=1 ISEQ=1 NVLLH=1')
 833    FORMAT(' ERROR IN INPUT DATA ISEQ=2 NVLLH=0')
 823    FORMAT(' ERROR IN INPUT DATA NVLLH=1 AND WATER CALCULATION')
 803    FORMAT(' ERROR IN INPUT DATA NVLLH=1 AND NSTRUC=0')
 100    FORMAT(2(F5.0,1X),I1,1X,10(F5.0,1X))
 111    FORMAT(2(F5.0,1X),I1,1X,11(F5.0,1X))
 180    FORMAT(4(F5.0,1X),I1,1X, 9(F5.0,1X))
 181    FORMAT(4(F5.0,1X),I1,1X, 9(F5.0,1X))
 101    FORMAT(100('-'),/,30X,'EXPERIMENTAL HYDRATE DATA',
     */,100('-'),/,4X,'PRESSURE',3X,'TEMPERATURE',
     *2X,'STRUCTURE',4X,10(A5,3X))
 102    FORMAT(3X,2(F10.3,4X),4X,I1,4X,10(F7.4,1X))
 103    FORMAT(4X,'PSIA',7X,'DEG.R',/,100('-'),//)
 105    FORMAT(100('-'),/,6X,'INPUT HYDRATE DATA
```

```
     A WITH INITIAL PRESSURE GUESSED',
     B/,100('-'),/,'PRESSURE',3X,'TEMPERATURE',
     C2X,'STRUCTURE',10(8X,A5))
  200   FORMAT(5(I1,1X))
  202   FORMAT(I2)
  301   FORMAT(20X,5('*'), 1X,'1 = METHANE'/,20X,5('*'),1X,'2 = ETHANE'
     *  ,/,20X,5('*'),1X,'3 = ETHYLENE',/,20X,5('*'),1X,'4 = PROPANE
     *  ',/,20X,5('*'),1X,'5 = CYCLO-PROPANE',/,20X,5('*'),1X,
     *  '6 = N-BUTANE
     * ',/,20X,5('*'),1X,'7 = ISO-BUTANE',/,20X,5('*'),1X,
     *  '8 = CYCLO-BUTANE
     * ',/,20X,5('*'),1X,'9 = PENTANE',/,20X,5('*'),1X,'10 = ISO-PENTANE
     * ',/,20X,5('*'),1X,'11 = NEO-PENTANE',/,20X,5('*'),1X,'12 =
     * CYCLO-PENTANE
     * ',/,20X,5('*'),1X,'13 = WATER',/, 20X,5('*'),1X,
     *  '14 = HYDROGEN',/,20X,5('*'),1X,
     *  '15 = CARBON-DI-OXIDE',/,20X,5('*'),
     *  1X,'16 = OXYGEN',/,20X,5('*'),1X,'17 = NITROGEN',/,20X,5('*'),
     * 1X,'18 = HYDROGEN SULFIDE',/,20X,5('*'),1X,'19 = XENON',/,20X,
     * 5('*'),1X,'20 = ARGON',/,20X,5('*'),1X,'21 = KRYPTON',/,
     * 20X,5('*'),1X,'22 = SULFUR HEXAFLOURIDE',/,20X,5('*'),1X,'
     *23 = CIS-2-BUTENE',/,20X,5('*'),1X,'24 = TRANS-2-BUTENE',/,20X
     * ,5('*'),1X,'25 = NO COMPONENT',///)
  302   FORMAT(8(I1,1X))
  330   FORMAT(2(F5.0,1X),I1,1X,11(F5.0,1X))
  329   FORMAT(2(F5.0,1X),I1,10(F5.0,1X))
  305   FORMAT(I2)
  306   FORMAT(10X,5(2X,E12.5),/,10X,5(2X,E12.5),/,10X,5(2X,E12.5),/
     1 ,10X,5(2X,E12.5))
  307   FORMAT(10X,6(2X,E12.5),/,10X,6(2X,E12.5),/,10X,6(2X,E12.5),/,
     1  10X,6(2X,E12.5),/,12X,E12.5)
  308   FORMAT(1(/),10(I2,1X))
  310   FORMAT(10X,'COMPONENT',I2,'=',A5)
  315   FORMAT(100('-'),/)
  812   FORMAT(///,25('*'),5X,' VALUES USED TO CALCULATE PRESSURES',
     15X,25('*'),///,' SIGMA,H2O SC..............',F10.5,/,
     2' EPSILON,H2O ................',F10.5,/,
     3' DELTA U .....................',F10.5,/,
     4' DELTA H .....................',F10.5,/,
     5' BETA ........................',F10.5,/,
     6' GAMMA .......................',F10.5,/,
     7' SIGMA  H20 LC  ..............',F10.5,///)
        GO TO 1000
 1002   WRITE(6,803)
        GO TO 1000
 1003   WRITE(6,823)
        GO TO 1000
 1004   WRITE(6,833)
        GO TO 1000
 1005   WRITE(6,843)
        GO TO 1000
 1006   WRITE(6,853)
*1000   END
1000    stop
        end
C
C
```

```
C
C
C       ****************************************************
             SUBROUTINE FUN(NN,XX,FF)
C       ****************************************************
C
C         THIS PROGRAM CALCULATES THE DIFFERENCES BETWEEN
C       EXPERIMENTAL AND THEORETICAL HYDRATE FORMING
C       CONDITIONS.  THE CALCULATED HYDRATE FORMING CONDITIONS
C       DEPEND UPON THE CHOICE OF KIHARA PARAMETERS
C       , SIGMA AND EPSILON, FOR THE VARIOUS COMPONENTS IN
C       THE GAS PHASE.
C
C
C       HYDRATE PHYSICAL PROPERTIES ARE ASSIGNED. SUBROUTINE DATA
C       IS CALLED TO READ GAS PROPERTIES. SUBROUTINE HYDRAT IS
C       CALLED TO CALCULATE HYDRATE FORMING CONDITIONS OR SUB-
C       ROUTINE QUAD IS CALLED FOR QUADRUPLE POINT CALCULATIONS
C       OR FOR SEQUENTIAL CALCULATIONS.
C
C
C       ************ COMMON STATEMENTS  ************
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
       DIMENSION ICODE(10)
       DIMENSION KK(10),XA(11)
       DIMENSION XX(13),PCALC(100),SS(100),AXC(10,2),Y(10)
       DIMENSION ERROR(100)
       DIMENSION A(10),SIGMA(10),EPS(10)
       DIMENSION Y3(100)
       DIMENSION ERR(100),SW(100)
       DIMENSION XL(10)
       DIMENSION NCODE(10)
       DIMENSION GAMMA1(2)
       DIMENSION ZZV(100)
       COMMON/BKSB/NPT,NSETS,IFLAG
       COMMON/STAT/SS
       COMMON/NC/NCODE,NCOMP
       COMMON/AMOL/MA,ISCODE(10)
       COMMON/FUND/SIGMA,EPS,A
       COMMON/TEXPT/PEXP(100),X(15,100),IS(100),T(100),YEXP(100)
       COMMON/SERDAT/T1(100),DT(100),T2(100)
       COMMON/DHDATA/DU(2),DH(2)
       COMMON/AZ/KK,N,MK
       COMMON/JK/JCHK
       COMMON/BEGA/BETA1,GAMMA1
       COMMON/COR/EPSH,DDU,DDH,BETA,GAMMA
       COMMON/VDO/SIGH1,SIGH2
       COMMON/BKSC/IWATER,IPOS,ISTR,IDH
       COMMON/HO/YH3
       COMMON/X/XL
       COMMON/PHAS/NVLLH
       COMMON/STRUC/NSTRUC
       COMMON/IMP/IMPURE,IMCODE,XIMP(100),YCO2(100)
       COMMON/SOLUT/XSOLU,ACTIV,YYYCO2
       COMMON/TBLOC/ITAG
       COMMON/SEQ/ISEQ,TMIN,DELT,TMAX,TQL
       COMMON/LIQUID/LIQ
```

```
      COMMON/ZV/ZV
      COMMON/HEAT/DDELH(100),DELH
C     ******************************************
      IF(IWATER.EQ.0)GO TO 105
      IF(IWATER.EQ.1)GO TO 102
      WRITE(6,104)
      GO TO 105
 102  WRITE(6,103)
 105  CONTINUE
      N=NPT
      SUM=0.0
      WSUM=0.0
      IF(ISEQ.EQ.1.OR.ISEQ.EQ.2)GO TO 80
      IF(NVLLH.EQ.0)GO TO 80
      IF(NSTRUC.EQ.2)GO TO 845
      IF(LIQ.EQ.0)WRITE(6,201)
      IF(LIQ.EQ.1)WRITE(6,2011)
      GO TO 80
 845  WRITE(6,202)
 80   CONTINUE
      DO 9 K=1,N
C     REFERENCE PARAMETERS FOR STRUCTURE I AND II
      SIGH1=3.56438
      SIGH2=SIGH1
      EPSH=102.13357
      DU(2)=222.371
      DDU=DU(2)
      DH(2)=300.984
      DDH=DH(2)
      BETA1=0.0
      BETA=BETA1
      GAMMA1(2)=-0.00045
      GAMMA=GAMMA1(2)
4     CONTINUE
      SIGH1=3.56438
      SIGH2=SIGH1
      EPSH=102.13357
      DU(1)=267.74141
      DDU=DU(1)
      DH(1)=301.32093
      DDH=DH(1)
      BETA1=0.0
      BETA=BETA1
      GAMMA1(1)=-0.00145
      GAMMA=GAMMA1(1)
 3    CONTINUE
      DO 10 KI=1,MA
      Y(KI)=0.0
 10    CONTINUE
      DO 101 I=1,MA
      Y(I)=X(I,K)
  101 CONTINUE
      XSOLU=XIMP(K)
      YYYCO2=YCO2(K)
      CALL DATA(Y,XA,T(K))
      DO 901 I=1,MA
 708  Y(I)=XA(I)
```

```
      EPS(I)=(EPS(I)*EPSH)**0.5
      SIGMA(I)=0.5*(SIGMA(I)+SIGH1)
 901  CONTINUE
      PCALC(K)=PEXP(K)
      IF(NVLLH.EQ.0.AND.ISEQ.EQ.0)GO TO 79
      IF(ISEQ.EQ.0)GO TO 846
      T(K)=T1(K)
      TMIN=T1(K)
      DELT=DT(K)
      TMAX=T2(K)
846   CALL QUAD(T(K),PCALC(K),Y,IS)
      GO TO 9
79    ITAG=0
      IF(LIQ.EQ.1)ITAG=2
        CALL HYDRAT( T(K), PCALC(K), Y, AXC, IS(K))
      Y3(K)=YH3
      DDELH(K)=DELH
      ZZV(K)=ZV
      PCALC(K)=PCALC(K)*6.8948
      PEXP(K)=PEXP(K)*6.8948
      T(K)=T(K)/1.8
      IF(IWATER.EQ.1)GO TO 9
      IF(IWATER.EQ.2)GO TO 905
      ERROR(K)=ABS(PCALC(K)-PEXP(K))*100.0/PEXP(K)
      SS(K)=(1.0-PCALC(K)/PEXP(K))**2
      SUM=SUM+SS(K)
      GO TO 9
905   ERR(K)=ABS(Y(IPOS)-YEXP(K))*100.0/YEXP(K)
      SW(K)=(1.0-Y(IPOS)/YEXP(K))**2
      WSUM=WSUM+SW(K)
      WRITE(6,909)T(K),PEXP(K),Y(IPOS),YEXP(K),ERR(K),PCALC(K),Y3(K)
9      CONTINUE
      IF(NVLLH.NE.0)GO TO 960
      IF(ISEQ.NE.0)GO TO 960
      IF(IWATER.EQ.2)GO TO 906
      IF(IWATER.EQ.1)GO TO 960
      FF=SUM/N
      FF=(FF**0.5)*100.0
      IF(IFLAG.EQ.0)GO TO 950
      IF(IDH.EQ.0) GO TO 435
      IF(IDH.EQ.1) WRITE(6,778)
      DO 434 K=1,N
      WRITE(6,779) T(K),PCALC(K),DDELH(K),ZZV(K),(X(J,K),J=1,MA)
434   CONTINUE
435   CONTINUE
      IF(IDH.EQ.1) GO TO 962
      WRITE(06,902)
      DO 913 K=1,N
      WRITE(06,900)T(K),PEXP(K),PCALC(K),ERROR(K),IS(K)
913   CONTINUE
      WRITE(6,206)FF
      GO TO 960
906   YFF=WSUM/N
      YFF=(YFF**0.5)*100.0
      WRITE(6,908)YFF
      GO TO 960
950   WRITE(6,951)
```

```
        DO 952 K=1,N
        WRITE(6,953)T(K),PCALC(K)
 952    CONTINUE
 962    CONTINUE
C
C      * * FORMAT STATMENTS * *
C
 778    FORMAT(///20X,'CALCULATED RESULTS'//1X,'TEMPERATURE',3X,
     1  'PRESSURE',4X,'DELTA H',13X,'Y-1',5X,'Y-2',5X,'Y-3'
     2  /5X,'(K)',8X,'(KPA)',5X,'(KJ/MOLE)',5X,'Z',/80('-'))
 779    FORMAT(2X,F6.2,5X,F8.2,6X,F6.2,4X,F6.4,2X,10(F6.4,2X))
 909    FORMAT(5X,F7.3,2X,F9.3,1X,F15.9,1X,F15.9,3X,F6.1,4X,':',2X,
     AF9.3,1X,F15.9)
 206    FORMAT(/,3X,'AVERAGE ERROR IS',3X,F6.2,'%')
 201    FORMAT(///20X,'CALCULATED RESULTS'//18X,'V L1 L2 H   QUADRUPLE
     1 POINTS'/70('-')/5X,'TEMP',7X,'PRESS',5X,'STRUC',5X,'LIQUID COMP
     1OSITION'/6X,'(K)',7X,'(KPA)',16X,'WATER FREE'/70('-')/)
 2011   FORMAT(///20X,'CALCULATED RESULTS'//18X,'V L1 L2 H   QUADRUPLE
     1 POINTS'/70('-')/5X,'TEMP',7X,'PRESS',5X,'STRUC',5X,'VAPOR  COMP
     1OSITION'/6X,'(K)',7X,'(KPA)',16X,10X/70('-')/)
 202    FORMAT(///,20X,'CALCULATED RESULTS',//,3X,'V H1 H2 L1  QUADRUPLE
     1 POINTS',3X,':',3X,'V L1 L2 H  QUADRUPLE POINTS',/,3X,28('-'),3X
     2,':',3X,28('-'),/,2X,'STRUCT',3X,'TEMP',8X,'PRESS',6X,':',6X,'TEMP
     3',8X,'PRESS',7X,'LIQUID COMPOSITION',/,2X,'BELOW',5X,'(K)',8X, '(K
     4PA)',6X,':',7X,'(K)',8X,'(KPA)',8X,'X1',7X,'X2',/,1X,'QUAD PT',
     526X,':',30X,'WATER FREE',/,3X,28('-'),3X,':',3X,28('-'),//)
 900    FORMAT(1X,4(F10.3,2X),8X,I1)
 902    FORMAT(///,20X,'CALCULATED RESULTS',/,20X,10('-'),
     *1X,7('-'),//,6X,'TEMP',8X,'PEXP',7X,'PCALC',7X,
     *'ERROR',7X,'STRUCTURE'/,6X,'(K)',9X,'(KPA)',6X,
     *'(KPA)',/,80('-'),//)
 951    FORMAT(///,20X,'CALCULATED RESULTS',/,20X,
     A  10('-'),1X,7('-'),//,21X,'TEMP',7X,
     B  'PCALC',/,21X,'(K)',8X,'(KPA)',/,18X,21('-'),
     C  //)
 953    FORMAT(19X,F10.3,2X,F10.3)
 908    FORMAT(' AVERAGE ERROR IN YH2O CALCULATION',F8.2)
 103    FORMAT(///20X,'CALCULATED RESULTS'/20X,18('-')//10X,'2-PHASE',
     A45X,'3-PHASE'/4X,36('-'),14X,22('-')/5X,'TEMP',6X,'PRESS',
     A10X,'Y-2PHASE',10X,':',9X,'PRESS',5X,'Y-3PHASE'/5X,'(K)',
     A9X,'(KPA)',9X,'H2O',14X,':',6X,'(KPA)',10X,'H2O'/)
 104    FORMAT(///20X,'CALCULATED RESULTS'/20X,18('-')//20X,'2-PHASE',
     A50X,'3-PHASE'/5X,60('-'),7X,25('-')/6X,'TEMP',7X,'PRESS',8X,
     A'YCALC',12X,'YEXP',8X,'ERROR',4X,':',4X,'PRESS',10X,'Y-3PHASE'
     A/7X,'(K)',7X,'(KPA)',9X,'H2O',15X,'H2O',16X,':',5X,'(KPA)',
     A11X,'H2O'/)
 960    RETURN
        END
C
C
C       ****************************************************
        SUBROUTINE QUAD(T,P,Y,IS)
C       ****************************************************
C
C      THIS SUBROUTINE CALCULATES QUADRUPLE POINTS BY FINDING THE
C      POINT OF INTERSECTION OF 'V L1 H' AND DEW POINT CURVES TO
C       GET THE 'V L1 L2 H' POINT ; OR INTERSECTION OF 'L1 L2 H'
```

```
C       AND BUBBLE POINT CURVE TO GET 'V L1 L2 H';
C        AND 'V L1 H1' AND 'V L1 H2'
C      CURVES TO GET THE 'V L1 H1 H2' POINT.
C
C       THIS SUBROUTINE IS ALSO CALLED FOR SEQUENTIAL CALCULATIONS
C       AT SPECIFIC INTERVALS.
C
C       IST0=STRUCTURE AT STARTING TEMP T0
C       IST2=STRUCTURE BEYOND THE QUAD POINT
C       ID=VARIABLE INDICATING WHETHER  VLH1H2 QUAD POINT HAS BEEN
C       CALCULATED. 0--NOT CALCULATED;  1--CALCULATED.
C       ITAG=VARIABLE INDICATING WHICH FUGACITY COEFFICIENTS ARE
C           REQUIRED FROM SUBROUTINE PHIMIX.  0--ONLY VAPOR
C                       1--VAPOR AND LIQ; 2--LIQUID ONLY.
C
         IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        DIMENSION Y(15),XL(10)
        DIMENSION PH(2),PRESS(2),ISCHEC(2),PBD(2),TQ(60),PQ(60)
        DIMENSION PLP2(60)
        DIMENSION PLP1(60)
        DIMENSION NCODE(10)
        COMMON/STRUC/NSTRUC
        COMMON/PHAS/NVLLH
        COMMON/X/XL
        COMMON/NC/NCODE,NCOMP
        COMMON/TBLOC/ITAG
        COMMON/SEQ/ISEQ,TMIN,DELT,TMAX,TQL
        COMMON/LIQUID/LIQ
        COMMON/CRITCL/NCRIT,TCRIT
        COMMON/HEAT/DDELH(100),DELH
        COMMON/BKSC/IWATER,IPOS,ISTR,IDH
        COMMON/ZV/ZV
        COMMON/HELP/IST0,IST2,ISLOW,N0,NQ
        DOUBLE PRECISION YNEW(100)
C
C
        T0=T
        ITER=0
        DTQ=1.0
        DTH=1.0
        N0=1
        AXC=0
        NQ=N0
        ID=0
        IDEW=0
        M=1
        IF(NVLLH.NE.0)GO TO 107
C
C       IF NVLLH IS ZERO THEN NO QUAD POINTS ARE REQUIRED BUT THIS
C       SUBROUTINE HAS BEEN CALLED FOR SEQUENTIAL CALCULATIONS.
C
        THH=TMAX+2.*DELT
        TQL=TMAX+2.*DELT
        IF(LIQ.EQ.1)TQL=TMIN-2*DELT
        GO TO 10
 107    DO 105 K=1,2
 17     IF(NSTRUC.EQ.2.AND.ID.EQ.0)GO TO 101
```

```
        PRESS(K)=P
        ITAG=0
        IF(LIQ.EQ.1)ITAG=2
        CALL HYDRAT(T,PRESS(K),Y,AXC,IS)
        IF(NCRIT.EQ.1)GO TO 801
        GO TO 103
 101    DO 102 IQ=1,2
        IS=IQ
        PH(IS)=P
        ITAG=0
        CALL HYDRAT(T,PH(IS),Y,AXC,IS)
        IF(NCRIT.EQ.1)GO TO 801
 102    CONTINUE
C
C  ** CHECK WHICH STRUCTURE IS FORMED AT TEMP T **
        IF(PH(2).LT.PH(1))IS=2
        IF(PH(1).LT.PH(2))IS=1
        IF(PH(1).EQ.PH(2))GO TO 130
        ISCHEC(K)=IS
 16     PRESS(K)=PH(IS)
C
C  ** IST0 IS THE STRUCTURE FORMED AT THE STARTING TEMP (GIVEN TEMP) **
        IF(NQ.EQ.N0)IST0=IS
        NQ=NQ+1
 103    CONTINUE
        CALL BUBDEW(T,PBD(K),Y)
        IF(LIQ.EQ.1)GO TO 140
        IF(PBD(K).GE.PRESS(K))GO TO 150
        IDEW=IDEW+1
        IF(IDEW.GT.5)T=T-1.0
        IF(IDEW.LT.5)T=T-0.4
        IF(IDEW.GT.20)GO TO 152
        GO TO 107
 140    IF(PBD(K).LT.PRESS(K))GO TO 150
        IDEW=IDEW+1
        IF(IDEW.LE.2)T=T+0.2
        IF(IDEW.GT.2)GO TO 110
        GO TO 107
 150    TCOMP=T
        IF((NSTRUC.EQ.1.OR.ID.EQ.1).AND.ABS(TQL-T).LT.5.0)GO TO 45
        IF(LIQ.EQ.0)T=T+1.0
        IF(LIQ.EQ.1)T=T-1.0
        IF(LIQ.EQ.0)DTQ=1.0
        IF(LIQ.EQ.1)DTQ=-1.0
        GO TO 105
 45     IF(LIQ.EQ.0)T=T+0.05
        IF(LIQ.EQ.1)T=T-0.1
        IF(LIQ.EQ.0)DTQ=0.05
        IF(LIQ.EQ.1)DTQ=-0.1
 105    CONTINUE
        IF(NSTRUC.EQ.1)GO TO 106
        IF(ID.EQ.1)GO TO 106
        IF(ISCHEC(1).EQ.ISCHEC(2))GO TO 106
        T=T-3
        GO TO 107
 106    AMH=(DLOG(PRESS(2))-DLOG(PRESS(1)))/DTQ
        CH=DLOG(PRESS(2))-AMH*(T-DTQ)
```

```
        AML=(DLOG(PBD(2))-DLOG(PBD(1)))/DTQ
        CL=DLOG(PBD(2))-AML*(T-DTQ)
        TQL=(CH-CL)/(AML-AMH)
        PQL=EXP(AMH*TQL+CH)
        IF(NSTRUC.EQ.1)GO TO 109
        IF(ID.EQ.1)GO TO 182
        IF(T.EQ.(T0+1))PQLOW=PQL
        IF(PQL.GT.PQLOW)GO TO 113
        PQLOW=PQL
        ISLOW=IS
 113    TQ(M)=TQL
        PQ(M)=PQL
        PLP1(M)=PRESS(1)
        PLP2(M)=PRESS(2)
        IF(IS.NE.IST0)GO TO 111
        IF(T.GT.TQL)GO TO 120
        M=M+1
        IF(M.EQ.50)GO TO 112
        GO TO 107
C    **IF IST0=ISLOW NO VLHH PRESENT **
 111    IF(IST0.EQ.ISLOW)GO TO 114
        IST2=IS
        AM1=(DLOG(PLP2(M-1))-DLOG(PLP1(M-1)))/DTH
        AM2=(DLOG(PLP2(M))-DLOG(PLP1(M)))/DTH
        C1=DLOG(PLP2(M-1))-AM1*(T-3)
        C2=DLOG(PLP2(M))-AM2*(T-1)
        THH=(C1-C2)/(AM2-AM1)
        PHH=EXP(AM2*THH+C2)
 182    ID=1
        IF(ABS(TQL-TCOMP).LE.0.1)GO TO 181
        ITER=ITER+1
        IF(ITER.GT.500)GO TO 151
        T=(TQL+TCOMP)/2.0
        GO TO 107
 181    CONTINUE
        IF(ISEQ.EQ.1.OR.ISEQ.EQ.2)GO TO 10
        THH=THH/1.8
        TQL=TQL/1.8
        PHH=PHH*6.8948
        PQL=PQL*6.8948
        WRITE(6,203)IST0,THH,PHH,TQL,PQL,(XL(I),I=1,NCOMP)
        GO TO 120
 114    WRITE(6,117)
        TQ(1)=TQ(1)/1.8
        PQ(1)=PQ(1)*6.8948
        WRITE(6,118)IST0,TQ(1),PQ(1),(XL(I),I=1,NCOMP)
        GO TO 120
 109    IF(ABS(TQL-TCOMP).LE.0.1)GO TO 110
 455    ITER=ITER+1
        IF(ITER.GT.500)GO TO 151
        T=(TQL+TCOMP)/2.0
        IF(LIQ.EQ.1)T=TCOMP
        GO TO 107
 110    IF(ISEQ.EQ.0)GO TO 104
 10     T=TMIN-DELT
        DO 257 J = 1,NCOMP
        YNEW(J) = Y(J)
```

```
 257     CONTINUE
        IF(NSTRUC.EQ.2)IS=IST0
C
C    ** CHECK FOR HEAT OF DISSOCIATION CALCULATIONS **
C
        IF(LIQ.EQ.0.AND.IDH.EQ.0)WRITE(6,250)
        IF(LIQ.EQ.1)WRITE(6,2501)
        IF(IDH.EQ.1)WRITE(6,886)
        ITAG=0
        IF(T.GT.TQL)ITAG=2
        IF(ISEQ.EQ.2)TMAX=TQL
        IF(ISEQ.EQ.2.AND.LIQ.EQ.1)GO TO 853
        DO 91 I=1,100
        T=T+DELT
        IF(T.GT.TMAX)GO TO 120
        CALL HYDRAT(T,P,YNEW,AXC,IS)
        TT=T/1.8
        PP=P*6.8948
        IF(IDH.EQ.0) GO TO 14
        WRITE(6,885) TT,PP,DELH,ZV,(YNEW(N),N=1,NCOMP)
        GO TO 8567
 14     CONTINUE
        IF(T.LT.TQL)WRITE(6,904)TT,PP,IS,(YNEW(N),N=1,NCOMP)
        IF(T.GT.TQL)WRITE(6,904)TT,PP,IS,(XL(N),N=1,NCOMP)
 8567   CONTINUE
        TTHH=THH/1.8
        PPHH=PHH*6.8948
        IF(NSTRUC.EQ.2.AND.(T+DELT).GT.THH)IS=IST2
        IF(NSTRUC.EQ.2.AND.T.LT.THH.AND.(T+DELT).GT.THH)WRITE(6,153)
     1TTHH,PPHH
        IF((T+DELT).GE.TQL)GO TO 191
        GO TO 91
 191    PPQL=PQL*6.8948
        TTQL=TQL/1.8
        IF(T.LT.TQL.AND.(T+DELT).GE.TQL.AND.ISEQ.NE.2)WRITE(6,71)TTQL
     1,PPQL
        IF(T.LT.TQL.AND.(T+DELT).GE.TQL.AND.ISEQ.EQ.2)WRITE(6,72)TTQL
     1,PPQL
        ITAG=2
        IF(LIQ.NE.0)GO TO 91
        DO 53 J=1,NCOMP
        Y(J)=XL(J)
  53    CONTINUE
 91     CONTINUE
        WRITE(6,123)
        GO TO 120
 104    TQL=TQL/1.8
        PQL=PQL*6.8948
        WRITE(6,444)(XL(I),I=1,NCOMP)
        WRITE(6,444)(Y(J),J=1,NCOMP)
 444    FORMAT(' XL=',10(4X,F6.3))
C
        WRITE(6,119)TQL,PQL,IS,(XL(I),I=1,NCOMP)
        GO TO 120
 112    WRITE(6,121)
        GO TO 114
 130    WRITE(6,108)PH(1)
```

```
 120    T=T0
        GO TO 800
 151    WRITE(6,100)
        GO TO 800
 152    TQL=TQL/1.8
        PQL=PQL*6.8948
        WRITE(6,154)TQL,PQL
        GO TO 800
 853    WRITE(6,823)
        DO 258 I=1,NCOMP
        Y(I)=YNEW(I)
 258    CONTINUE
C  ---------FORMATS-----------------
 885    FORMAT(1X,F6.2,3X,F8.2,4X,F7.3,5X,F6.4,4X,10(F6.4,2X))
 886    FORMAT(///25X,'CALCULATED RESULTS',////3X,'TEMP',4X,'PRESSURE'
     2  ,3X,'DELTA H',8X,'Z',10X,'GAS COMPOSITION',/4X,'(K)',6X,'(KPA)'
     3  ,4X,'(KJ/MOLE)',15X,'Y-1',5X,'Y-2',5X,'Y-3'/80('-'))
 121    FORMAT(' NOT CONVERGED IN QUAD, PROBABLY NO  V L H1 H2  EXISTS')
 100    FORMAT(' QUADRUPLE POINT CALCULATIONS NOT CONVERGED IN QUAD
     1. INITIAL TEMP MAY NOT BE IN RANGE.')
 119    FORMAT(4X,F6.2,5X,F9.2,4X,I1,5X,10(F6.4,5X))
C901    FORMAT(2F,I,'FOR901')
 118    FORMAT(4X,I1,35X,F6.2,5X,F8.2,5X,10(F6.4,5X))
 203    FORMAT(4X,I1,5X,F6.2,5X,F8.2,5X,':',5X,F6.2,5X,F8.2,5X,10(F6.4
     1,5X))
 123    FORMAT(1X,40('-'))
 250    FORMAT(///20X,'CALCULATED RESULTS'/20X,10('-'),1X,7('-')/10X,
     1'TEMP',10X,'PRESS',4X,'STRUCTURE',8X,'GAS COMPOSITION',/11X,
     1'(K)',10X,'(KPA)',16X,'Y 1',4X,'Y 2',4X,'Y 3'/5X,60('-'))
 2501   FORMAT(///20X,'CALCULATED RESULTS'/20X,10('-'),1X,7('-')/10X,
     1'TEMP',10X,'PRESS',7X,'STRUCTURE',5X,'LIQ COMPOSITION',/11X,
     1'(K)',10X,'(KPA)',16X,'XL1',5X,'XL2',5X,'XL3'/5X,60('-'))
 904    FORMAT(9X,F6.2,8X,F8.2,6X,I3,3X,10(F6.4,2X))
 108    FORMAT(' QUAD PT AT PRESS=',F10.2)
 117    FORMAT(' V L H1 H2  EQUILIBRIUM  NOT PRESENT')
 153    FORMAT(9X,F6.2,8X,F8.2,2X,'QUADRUPLE POINT  V L H1 H2')
 71     FORMAT(9X,F6.2,8X,F8.2,2X,'QUADRUPLE POINT  V L1 L2 H'//53X,
     1'LIQUID COMPOSITION'/48X,'X 1',6X,'X 2',6X,'X 3'/)
 72      FORMAT(9X,F6.2,8X,F8.2,2X,'QUADRUPLE POINT  V L1 L2 H'/)
 154    FORMAT(/' NOT CONVERGED DUE TO TEMP CROSSING QUAD POINT'/' TQL='
     1,F6.2,2X,'PQL=',F8.2)
 823    FORMAT(' ERROR IN INPUT DATA ISEQ=2 AND LIQ=1')
 843    FORMAT(' QUAD POINT NOT CALCULATED'/' VAPOR IS
     1 CLOSE TO CRITICAL'/' CRITICAL TEMP OF MIX=',F6.2,'K'/)
C ------------------------------------------------------
        GO TO 800
 801    TCRIT=TCRIT/1.8
        WRITE(6,843)TCRIT
 800    RETURN
        END
C       ************************************************
C
C
C
C
C       ******************************************************
        SUBROUTINE HYDRAT(T,P,XU,VY,IS)
```

```
C       ******************************************************
C       PROGRAM FOR CALCULATION OF THE DISSOCIATION PRESSURES
C        OF GAS HYDRATES FROM METHANE, ETHANE, AND PROPANE
C        BY JERRY HOLDER, CHEMICAL ENGINEERING U. MICH.
C
C      THE DISSOCIATION PRESSURE IS THAT PRESSURE AT WHICH
C      THE CHEMICAL POTENTIAL OF WATER IN THE HYDRATE IS
C      EXACTLY EQUAL TO THE CHEMICAL POTENTIAL OF THE WATER
C      IN THE WATER PHASE.  THE CHEMICAL POTENTIAL OF THE
C      HYDRATED WATER IS CALCULATED USING THE THEORY DEVELOPED
C      BY VAN DER WAALS WHICH ASSUMES 1) THERE IS ONE MOLECULE
C      OF GAS PER HYDRATE CAVITY,  2) ONLY THE TRANSLATIONAL
C      PARTITION FUNCTION IS AFFECTED IN THE ENCAGED STATE
C      3)  ONLY FIRST NEIGHBOR INTERACTIONS ARE IMPORTANT.
C      THE KIHARA POTENTIAL MODEL IS USED.
C
C       THE UPDATED Q* VERSION INCLUDES 2ND AND 3RD SHELL
C       CONTRIBUTIONS AND SHELL ASPHERICITY.
C
C       THIS SUBROUTINE ALSO CALCULATES WATER CONTENT AND
C       HEAT OF DISSOCIATION.
C
C       *** LIST OF VARIABLES ***
C
C       AR, BR, CR - CONSTANTS FOR CALCULATING THE DISSOCIATION
C                    PRESSURE OF THE REFERENCE HYDRATE. THESE ARE
C                    FROM FITTED DATA.
C       C      -     THE SO CALLED LANGMUIR ADSORPTION CONSTANTS
C                    WHICH SPECIFY THE RELATIVE AMOUNT OF GAS IN
C                    A GIVEN TYPE OF CAVITY. SUBSCRIPTS I,J REFER
C
C       DH          - DIFFERENCE IN ENTHALPY BETWEEN THE OCCUPIED AND
C                     UNOCCUPIED HYDRATE.
C       DU          - DIFFERENCE IN CHEM. POTENIAL (AS DH)
C       DV          - DIFFERENCE IN MOLAR VOLUME
C       P0          - DISSOCIATION PRESSURE OF REFERENCE HYDRATE
C                     AT 273 DEG K
C       PR          - DISSOCIATION PRESSURE OF REF. HYD. AT T
C       T           -TEMPERATURE( DEG K)
C                       (NOTE THAT T IS CHANGED FROM R TO K )
C       VM          - NUMBER OF MOLECULES OF WATER PER CAVITY
C       VY(I,J)     - FRACTION OF CAVITIES I OCCUPIED BY MOLECULE J
C       XU(I)       - MOLE FRACTION OF GAS I IN THE GAS PHASE
C       ZMU,ZMOLD, ETC. - CHEMICAL POTENTIAL DIFFERENCES.
C
C
C     ************   COMMON STATEMENTS    *************

      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C     external psat
      DIMENSION KK(10)
      DIMENSION XX(13)
      DIMENSION XL(10),PHIL(10)
      DIMENSION XU(10),PHI(10),XS(10),VY(10,2),VM(2),
     2 C(10,2),NCODE(10),SCC(2)
      DIMENSION XXMAX(10),XXMIN(10),B2(10)
        DIMENSION XW(10)
```

```
        DIMENSION GAMMA1(2)
        DIMENSION XHYD(10)
        DIMENSION VVY(2)
      COMMON /PVDATA/ DV,AR,BR,CR
      COMMON/AZ/KK,N,MK
      COMMON/AMOL/MA,ISCODE(10)
      COMMON/NC/NCODE,NCOMP
      COMMON/MAMI/XXMAX,XXMIN
      COMMON /HYD/ IHYD
      COMMON/FUND/SIGMA(10),EPS(10),A(10)
      COMMON/DHDATA/HDU(2),HDH(2)
      COMMON/JK/JCHK
      COMMON/VDO/SIGH1,SIGH2
      COMMON/BEGA/BETA1,GAMMA1
      COMMON/BKSC/IWATER,IPOS,ISTR,IDH
        COMMON/TBLOC/ITAG
        COMMON/HO/YH3
        COMMON/SOLUT/XSOLU,ACTIV,YYYCO2
        COMMON/IMP/IMPURE,IMCODE,XIMP(100),YCO2(100)
        COMMON/TFREEZ/TT0
        COMMON/ZV/ZV
        COMMON/X/XL
        COMMON/PH/PHIL
        COMMON/WATER/NW
        COMMON/STOR/XUSTOR(10)
        COMMON/CRITCL/NCRIT,TCRIT
        COMMON/HEAT/DDELH(100),DELH
        COMMON/HELP/IST0,IST2,ISLOW,NQ,N0
C
C       ************************************************
C
C
C      * * CHECK IF STRUCTURE DATA IS TO BE PRINTED * *
C
        JACKQ=0
C     Saturation pressure is in atmospheres.  Partial molar volume isin

      ml/mole.  Saturation pressure is the pressure at which a giv
C     mole fraction of gas is dissolved in the liquid.
      PSATD=30.30
      PMOLVOL=35.

 17     CONTINUE
        IF(ITAG.NE.2)GO TO 40
        DO 43 I=1,NCOMP
        XL(I)=XU(I)
 43     CONTINUE
 40     IF(ISTR.NE.1)GO TO 260
        WRITE(06,351)
        DO 258 I=1,MA
        WRITE(06,352)KK(I),A(I),SIGMA(I),EPS(I)
 258    CONTINUE
C
 260  DO 5 I=1,NCOMP
      DO 5 J=1,2
    5 VY(I,J)=0.0
      T=T/1.8
```

```
      PSAVE=P
      P=P/14.696
      IF( IS.EQ.1) GO TO 11
C
C        *** DATA FOR STRUCTURE II
C
      VM(1)=0.11765
      VM(2)=0.058823
      DV=4.99644
        IF(T.LE.(273.15-TT0)) DV=DV-1.6
        DU=HDU(2)
        DH=HDH(2)
        GAMMA=GAMMA1(2)
       GO TO 12
C
C        *** DATA FOR STRUCTURE I ***
C
 11   VM(1)=2./46.
      VM(2)=6./46.
      DU=HDU(1)
      DH=HDH(1)
      DV=4.5959
        GAMMA=GAMMA1(1)
        IF(T.LE.(273.15-TT0)) DV=DV-1.6
C
C       *** LANGMUIR CONSTANTS
C
   12 DO 15 K=1,NCOMP
      DO 15 J=1,2
       J5=J
       K5=K
       K1=K
 777    CONTINUE
       C(K,J)=CC(T,IS,J5,K5,K1)
 15     CONTINUE
C
C
C           AT ZERO DEGREES CENTIGRADE
C
        ZMUTPR=DU/273.15
        ZMOLD=ZMUTPR
        AH=2616.398+DH
        TO=273.15
C
C      *** ENTHALPIC CHANGE OF CHEMICAL POTENTIAL WITH
C          TEMPERATURE (WATER PHASE)
C
C ***** ALPHA, BETA, AND GAMMA ARE PARAMETERS *****
C *****      IN THE ENTHALPIC INTEGRAL       *****
        IF(T.GT.273.1.AND.T.LT.273.2) GO TO 8999
        ALPHA=DH
        BETA=BETA1
        IF(T.LT.(273.15-TT0)) GO TO 8998
        ALPHA=ALPHA-1436.0+9.054*273.15+0.021163*(273.15**2)
        BETA=BETA+9.054+0.042326*273.15
        GAMMA=GAMMA-0.021163
 8998   CONTINUE
```

```
        HINT=ALPHA*(1./T-1./273.15)+BETA*DLOG(T/273.15)
     *  +GAMMA*(T-273.15)
        GO TO 9988
 8999   HINT=0.0
 9988   CONTINUE
C
C
C       *** VOLUMETRIC CHANGE OF CHEMICAL POTENTIAL WITH
C       TEMPERATURE (DP=DP/DT*DT)
C       GAUSSIAN INTEGRATION IS USED.
        ZM=HINT+ZMOLD
        ZMUTPR=T*ZM
C     We know that ZMUTPR is the liquid phase chemical potential
C     Instead of having the program calculate the pressure point where
C     the liquid phase chemical potential and the hydrate phase chemical
C     potentials intersect, we need to calculate the plain hydrate and
C     liquid potential.  We also need to print out ZMUPTR since it is
C     the liquid phase potential.
C       **** NEWTONS METHOD IS USED TO FIND THE PRESSURE AT
C            WHICH THE CHEMICAL POTENTIAL OF THE HYDRATED
C            AND LIQUID WATER ARE THE SAME (FOR THE SPECIFIED
C            TEMPERATURE).
C
C
      P1=1
      P2=2
       DO 30 JJ=1,2000
      DMU1=0.0
      DMU2=0.0
C     DO 28 JJJ=1,2
       P=P1
      P3=P
      IF (P.GT.PSATD) P3=PSATD
C       IF(JJJ.EQ.2) P=P2
C       *** GET THE FUGACITY COEFFICIENTS( PHI IS RETURNED)
C
C
      CALL PHIMIX(XU,14.696*P3,1.8*T,PHI)
        IF(NCRIT.EQ.1)GO TO 821
        IF(ITAG.NE.2)GO TO 481
C        DO 44 LI=1,NCOMP
C        PHI(LI)=PHIL(LI)
C 44     CONTINUE
        X1=0.0
        GO TO 56
 481    X1=0.0
       IF(T.LT.(273.15-TT0)) GO TO 56
       DO 55 J7=1,NCOMP
       KJ=NCODE(J7)
       Y7=XU(J7)
       PHI7=PHI(J7)
       CALL SOL7(KJ,Y7,PHI7,P3,T,X6)
       X1=X1+X6
  55   CONTINUE
  56   CONTINUE
      IF(ABS(P).LT. .1) P=P+.1
      ZMUA=ZMUTPR+DV/41.2929*(P)
```

```
      ZMUA=ZMUA-1.987*T*DLOG(1-X1)
C      WRITE(6,8890)ZMUA
      ZMU=0.0
       DO 27 I=1,2
       CCC=0.0
       DELTAP=0
       IF(P.GT.PSATD)DELTAP=P-PSATD
       DO 26 II=1,NCOMP
       FUGAC=PHI(II)*P3*DEXP(PMOLVOL*DELTAP/(82.1*T))
       CCC=CCC+ C(II,I)*XU(II)*FUGAC
       WRITE(6,5000)FUGAC
       WRITE(6,5001)PSATD
 5000  FORMAT(5X,'FUGACITY=',F10.5)
 5001  FORMAT(5X,'PSAT=',F10.5)
C      Need to obtain exact value of R with more precision than 82
   26  CONTINUE
      SCC(I)=CCC
C
C       *** POTENTIAL DIFFERENCE OF HYDRATE WATER
C
      IF(CCC.GT.-0.9) GO TO 461
      WRITE(6,457) CCC,C(1,1),XU(1),PHI(1),P
 457   FORMAT(5F10.2)
 461   CONTINUE
      ZMUTP=1.987*T*DLOG(1.+CCC)*VM(I)
C     WRITE(6,8891)ZMUPT
   27 ZMU=ZMUTP+ZMU
C       DMU=ZMUA-ZMU
C        IF(IMPURE.EQ.0.OR.T.LT.(273.15-TT0).OR.XSOLU.EQ.0.0)GO TO 148
C        DMU=DMU-1.987*T*DLOG(ACTIV*(1.0-XSOLU-X1))
C        GO TO 147
C 148    DMU=DMU-1.987*T*DLOG(1.0-X1)
C     ZMUA1=ZMUA-1.987*T*DLOG(1.0-X1)
C 147    DMU1=DMU2
C      DMU2=DMU
C
C      *** CHECK TO SEE IF CHEMICAL POTENTIALS ARE EQUAL
C          IF NOT, EXTRAPOLATE(OR INTERPOLATE) TO A NEW PRESSURE
C
C     IF(ABS(P2/P1-1.).LT..001.AND.ABS(DMU).LT.1.) GO TO 35
C     IF(ABS(DMU).LT..0005) GO TO 35
   28 CONTINUE
C     IF(ABS((P1-P2)/P2).LT.1.E-5) P2= P2+1.0
C     IF(ABS(DMU2-DMU1).LT. .001) GO TO 29
C     P3=P1-(P2-P1)/(DMU2-DMU1)*DMU1
C     IF(P3.LE.0.0) P3=0.01
C     IF(P3.GT.2.E4) P3=2.E4
C      P1=P3
C   29 P3=P1+3
   29 P2=P1+2
      Pold=P1
      P1=P1+1
      P=P1
      WRITE(6,8880)T
      WRITE(6,8881)Pold
      WRITE(6,8882)X1
      WRITE(6,8883)XSOLU
```

```
C     WRITE(6,8884)TT0
      WRITE(6,8885)ACTIV
      WRITE(6,8886)ZMU
      WRITE(6,8887)ZMUA
   30 CONTINUE
      GO TO 45
      IHYD=IS
      P=P1
      WRITE(6,505) DMU, IS,XU(1),T
  505 FORMAT(' FAILED TO CONVERGE IN HYDRATE',/,6X,
     2 'DIFFERENCE IN CHEMICAL POTENTIAL OF WATER',/,
     3 'IN THE HYDRATE AND WATER PHASES IS',2X,
     4 E9.2/,' STRUCTURE IS',I4,2F10.5)
   35 CONTINUE
 8880   FORMAT(5X,'T=',F10.5)
 8881   FORMAT(5X,'P=',F10.5)
 8882   FORMAT(5X,'X1=',F10.5)
 8883   FORMAT(5X,'XSOLU=',F10.5)
C 8884   FORMAT(5X,'TTO=',F10.5)
 8885   FORMAT(5X,'ACTIV=',F10.5)
 8886   FORMAT(5X,'ZMU=',F10.5)
 8887   FORMAT(5X,'ZMUA=',F10.5)
C 8888   FORMAT(5X,'XU(1)=',F10.5)
C 8889   FORMAT(5X,'XU(2)=',F10.5)
 8890   FORMAT(5X,'Chemical potential of liquid phase =',F10.5)
 8891   FORMAT(5X,'Chemical potential of the hydrate phase =',F10.5)
C      *** CALCULATE FRACTIONAL OCCUPANCY OF THE CAVITY
C
      DO 45 I=1,2
      DO 45 J=1,NCOMP
      IF(ABS(1+SCC(I)).LT.1.E-4) WRITE(6,9876) SCC(I)
 9876 FORMAT(' ERROR IN LANGMUIR CALCULATION',F10.7)
      VY(NCODE(J),I) = C(J,I)*XU(J)*PHI(J)*P/(1+SCC(I))
   45 CONTINUE
        IF(IDH.EQ.0) GO TO 46
C
C    ** HEAT OF DISSOCIATION CALCULATIONS **
C
        JACKQ=JACKQ+1
        IF(JACKQ.EQ.2) GO TO 412
        PH1=P
        TH1=T
        T=T+0.01
        T=T*1.8
        P=P*14.696
        GO TO 17
 412    CONTINUE
        JACKQ=0
        VVY(1)=0.0
        VVY(2)=0.0
        DO 7 J=1,NCOMP
        DO 7 I=1,2
        VVY(I)=VVY(I)+VY(NCODE(J),I)
 7      CONTINUE
        IF(IS.EQ.1) GO TO 717
        HN=136./(VVY(1)*16.+VVY(2)*8.)
        DV1=DV
```

```
        GO TO 718
 717    HN=46./(VVY(1)*2.+VVY(2)*6.)
 718    CONTINUE
C       WRITE(6,7777) ZV
C       WRITE(6,7778) T
C       WRITE(6,7779) TH1
C       WRITE(6,7780) P
C       WRITE(6,7781) PH1
C       WRITE(6,7782) VVY(1)
C       WRITE(6,7783) VVY(2)
C       WRITE(6,7784) HN
C       WRITE(6,7785) DV1
 7777   FORMAT(' ZV=',F10.5)
 7778   FORMAT(' T=',F10.5)
 7779   FORMAT(' TH1=',F10.5)
 7780   FORMAT(' P=',F10.5)
 7781   FORMAT(' PH1=',F10.5)
 7782   FORMAT(' VY(1)=',F10.5)
 7783   FORMAT(' VY(2)=',F10.5)
 7784   FORMAT(' HN=',F10.5)
 7785   FORMAT(' DV=',F10.5)
        DELHH=ZV*82.05*T**2*((DLOG(P/PH1))/(T-TH1))
        DELH2=HN*DV*T*((P-PH1)/(T-TH1))
        DELH=DELHH-DELH2
        DELH=DELH/9869.2
        DELHH=DELHH/9869.2
        DELH2=DELH2/9869.2
C       WRITE(6,7786) DELHH
C       WRITE(6,7787) DELH2
C       WRITE(6,7788) DELH
 7786   FORMAT(' DELH1=',F10.3)
 7787   FORMAT(' DELH2=',F10.3)
 7788   FORMAT(' DELH=',F10.3)
        T=TH1
        P=PH1
 46     CONTINUE
        COMSUM=0.0
        DO 143 J=1,NCOMP
        COMSUM=COMSUM+VY(NCODE(J),1)*VM(1)+VY(NCODE(J),2)*VM(2)
 143    CONTINUE
        DO 144 J=1,NCOMP
        XHYD(J)=(VY(NCODE(J),1)*VM(1)+VY(NCODE(J),2)*VM(2))/COMSUM
 144    CONTINUE
C       WRITE(7,1020)T,(VY(NCODE(J),1),VY(NCODE(J),2),J=1,MA)
 1020   FORMAT(' T (K)',4X,'HYDRATE COMPOSITION'/9X,'XH1   XH2'/
     1F6.2,4X,10(F6.4))
  700 T=T*1.8
      P=P*14.696
13    CONTINUE
C       WRITE(06,1005)
 1005     FORMAT(/,14X,'PHI(I)',20X,'LANGMUIR COEFFICIENTS'
     *  ,/,14X,5('-'),20X,21('-'))
        DO 158 I=1,NCOMP
C       WRITE(06,1008)PHI(I),(C(I,J),J=1,2)
C1008     FORMAT(5X,1F,10X,2F)
 158     CONTINUE
C
```

```
C       * * CALCULATIONS TO DETERMINE THE WATER CONTENT OF A GAS * *
C       * * IN EQUILIBRIUM WITH THE HYDRATE                       * *
C       * * TEMP(R) AND PRESSURE(PSIA)                           * *
C       * * IWATER = 0 : DONT PERFORM CALCULATIONS               * *
C       * * IWATER = 1 : CALCULATE YH2O
C       * * IWATER = 2 : CALCULATE YH2O AND COMPARE WITH EXPMTL DATA * *
C       * *                                                      * *
C
        IF(IWATER.EQ.0)GO TO 821
C
C       * * PH=3-PHASE PRESSURE * *
C       * * P =2-PHASE PRESSURE * *
C
C
        PH=P
        P=PSAVE
        PSW=PSAT(T)
        IF(IS.EQ.1)VHYD=22.6
        IF(IS.EQ.2)VHYD=22.9
        IF(T.LT.491.67)VH2O=19.6
        IF(T.GE.491.67)VH2O=18.0
        FWSAT=PSW*(1-X1)*EXP(0.0014926491/T*VH2O*(PH-PSW))
        FWSATP=FWSAT*EXP(0.0014926491/T*VHYD*(P-PH))
        CALL PHIMIX(XU,P,T,PHI)
        T=T/1.8
        P=P/14.696
        ZWAT=0.0
        DO 127 I=1,2
        CCC=0.0
        DO 126 II=1,NCOMP
        CCC=CCC+C(II,I)*XU(II)*PHI(II)*P
 126    CONTINUE
        ZW=VM(I)*DLOG(1+CCC)
 127    ZWAT=ZWAT+ZW
C
        DO 23 I=1,NCOMP
        XUSTOR(I)=XU(I)
 23     CONTINUE
        ICOUN=1
        COUNT=1
        MA=MA+1
        NCOMP=NCOMP+1
        IPOS=MA
        NW=1
        PHI(IPOS)=1.0
        PHIX=1.0
C**
        IF(14.696*P.GT.PH)GO TO 618
        GO TO 835
C
C       ** 2-PHASE WATER CONTENT CALCULATION **
 618    ZMUP=0.0
        GO TO 85
 85     FWP=FWSATP*DEXP(ZMU/(1.987*T)-ZWAT)
C
C       * * CALCULATE A TEST VALUE OF YH20 * *
        T=1.8*T
```

```
        P=14.696*P
C
 815       YH20N=FWP/(PHI(IPOS)*P)
        IF(YH20.GT.0.05.OR.YH20.LT.0.0)GO TO 800
        GO TO 801
 800    WRITE(6,803)ICOUN,YH20
        YH20=0.05
C
C
C
 801    XU(IPOS)=YH20N
        CALL NORMW(NCOMP,IPOS,XU)
        YH20=YH20N
 807   CALL PHIMIX(XU,P,T,PHI)
       YH20N=FWP/(PHI(IPOS)*P)
       ICOUN=ICOUN+1
        IF(ABS((YH20N-YH20)/YH20N).GT.1.E-3.AND.ICOUN.LT.30)GO TO 801
        XU(IPOS)=YH20N
C
C  **  3-PHASE WATER CONTENT CALCULATION  **
 835    DO 825 I=1,MA
        XW(I)=XU(I)
 825    CONTINUE
 809   YH3=FWSAT/(PHIX*PH)
        IF(ABS(YH3-XW(IPOS)).LT.1.E-7)GO TO 819
        XW(IPOS)=YH3
        CALL NORMW(NCOMP,IPOS,XW)
        CALL PHIMIX(XW,PH,T,PHI)
        COUNT=COUNT+1
        IF(COUNT.GT.30)GO TO 818
        PHIX=PHI(IPOS)
        GO TO 809
 818    WRITE(6,828)
 819    P2P=P*6.8948
        PH3P=PH*6.8948
        TK=T/1.8
       IF(ICOUN.GE.30)WRITE(6,810)
        IF(P.GT.PH)GO TO 845
        WRITE(6,823)
        GO TO 812
 845    IF(IWATER.EQ.2)GO TO 812
        WRITE( 6,811)TK,P2P,XU(IPOS),PH3P,YH3
C
 812    P=PH
        NCOMP=NCOMP-1
        MA=MA-1
        NW=0
 821    RETURN
C      * * FORMAT STATMENTS * *
C
 828    FORMAT(' 3 PHASE WATER CALCULATIONS NOT CONVERGED')
 803   FORMAT('0',T20,'* * YH20 DEFAULTS TO A VALUE OF 0.05 ON'
     A ,' ITERATION# ',I2,  / ,1X,T20,'* * FROM A PREVIOUS'
     B ,' VALUE OF YH20 = ',E10.3)
 810   FORMAT('0',T20,'* * WATER CONTENT EQUILIBRIUM
     C CALCULATIONS HAVE NOT CONVERGED * * ')
 811  FORMAT(5X,F7.3,2X,F9.3,2X,F15.9,8X,':',3X,F9.3,2X,F15.9)
```

```
 351  FORMAT(/,18X,'CODE #',5X,'A(I)',8X,'SIGMA(I)',8X,'EPS(I)',/)
 352  FORMAT(5X,I5,3F10.3)
 823    FORMAT(5X,' PRESSURE IS NOT IN 2 PHASE REGION')
C
      END
C
C
C
C     ******************************************************
      SUBROUTINE NORMW(NCOMP,IPOS,XU)
C     ******************************************************
C     * * THIS SUBROUTINE NORMALIZES THE VECTOR XU          * *
C     * * WITHOUT CHANGING THE VALUE OF XU(IPOS)            * *
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION XU(10)
      COMMON/STOR/XUSTOR(10)
C
      SUM=1.0-XU(IPOS)
      DO 1 I=1,NCOMP
      IF(I.EQ.IPOS)GO TO 1
      XU(I)=XUSTOR(I)*SUM
   1  CONTINUE
C
      RETURN
      END
C
C     ******************************************************
      DOUBLE PRECISION FUNCTION PSAT(TR)
C     ******************************************************
C     * * FUNCTION TO CALCULATE THE SATURATION PRESSURE OF  * *
C     * * WATER USING THE CORRELATION DEVELOPED BY KEENAN   * *
C     * * KEYES AND MOORE  P(PSIA), T(R)                   * *
C     * * A CORRELATION TO CALCULATE THE VAPOR PRESSURE     * *
C     * * FOR ICE WAS ALSO USED BASED ON THE DATA FROM      * *
C     * * PERRY'S 5'TH ED. 3-205                           * *
C     ******************************************************
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION F(8),A1(7),B1(7),TREF(8)
C
      DATA F/-741.9242,-29.721,-11.55286,-0.8685635,
     A0.1094098,0.439993,0.2520658,0.05218684/
C
      DATA A1/1.110788E-11,4.813026E-12,1.053791E-12,
     A6.92593447E-14,2.289828E-15,4.697288E-18,4.261011E-22/
C
      DATA B1/0.046341356,0.048066983,0.0512724161,
     A0.0572912243,0.06528872,0.08110062,0.108179821/
C
      DATA TREF/492.0,484.0,475.0,451.0,426.0,394.0,
     A344.0,300/
C
C
C     * * CRITICAL PROPERTIES FOR WATER * *
C
      T1=374.136
```

```
      P1=220.88
C
      C=TR/1.8-273.15
      AK1=1800.0/TR
C
C     * * CHECK IF LIQ. WATER OR ICE IS PRESENT  * *
C
      IF(TR.LT.492.0)GO TO 2
      P=0
      DO 1 J=1,8
   1  P=P+F(J)*(0.65-0.01*C)**(J-1)
      P=P1*DEXP(AK1*1.E-5*(T1-C)*P)/10.0
      PSAT=P*145.03894
      GO TO 40
C
C     * * CORRELATION FOR VAPOR PRESS. OF ICE         * *
C
   2  DO 10 I=1,7
      IF(TR.LE.TREF(I).AND.TR.GT.TREF(I+1))GO TO 20
  10  CONTINUE
      WRITE(6,30)TR
  20  PSAT=A1(I)*DEXP(B1(I)*TR)
C
  30  FORMAT(1X,T20,'* * TEMP BELOW TABLE FOR FUNCT. PSAT
     A: T(R)= ',E12.5)
C
C
  40  RETURN
      END

C
C
C       ******************************************************
        DOUBLE PRECISION FUNCTION CC(T,IS,IC,I,J)
C       ******************************************************
C
C
C
C       THIS FUNCTION CALCULATES LANGMUIR CONSTANTS FOR HYDRATE
C       FORMATION FROM C1,C2,OR C3 USING THE SPHERICALLY SYMETRIC
C       KIHARA POTENTIAL FUNCTION.  THIS PROGRAM CALLS ON THE
C       FUNCTION OMEGA WHICH GIVES THE POTENTIAL AS A FUNCTION OF
C       POSITION.   GAUSSIAN INTEGRATION (C&W PAGE 100) IS USED
C       TO INTEGRATE OMEGA OVER THE CELL VOLUME.
C       OMEGA IS A FUNCTION THAT CALCULATES THE
C       SMOOTHED CELL POTENTIAL AS A SUM OF
C       CONTRIBUTIONS OF THE FIRST,SECOND AND
C       THIRD SHELLS.
C       THE VARIABLES ARE
C       IS- CODE FOR WHICH HYDRATE STRUCTURE(I OR II) IS FORMED
C       IC= CODE FOR WHICH CAVITY IS UNDER CONSIDERATION
C       A= CORE RADIUS FOR THE MOLECULE,C1...C3
C       T=TEMPERATURE
C       EPS= EPSILON, DEPTH OF INTERMOLECULAR POTENTIAL WELL, ERG
C       R= RADIAL POSITION OF THE ENCLOSED MOLECULE
C       RR =FIRST SHELL RADIUS.
C       RR2=SECOND SHELL RADIUS
```

```
C       RR3=THIRD SHELL RADIUS.
C       Z=FIRST SHELL COORDINATION NUMBER
C       Z2=SECOND SHELL COORDINATION NUMBER.
C       Z3=THIRD SHELL COORDINATION NUMBER.
C
C       REF: PARRISH AND PRAUSNITZ,I&EC PROC. DES & DEV, 11(1),P26(1972)
C
C
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        EXTERNAL OMEGA
        COMMON /SIG/ SIGMA,EPS,RR,Z,A,TT,RR2,Z2,RR3,Z3
        COMMON /AMOL/MA,ISCODE(10)
        COMMON /RRR/ R
        COMMON/FUND/SSIG(10),EEPS(10),AA(10)
        COMMON/AFACT/OM(10)
        COMMON/ID/II,JJ,ISS
        CC=0.0
        II=I
        JJ=IC
        ISS=IS
C       WRITE(06,51)II,JJ,ISS,CC
 51       FORMAT(4X,3I2,5X,E15.5)
        PI=3.14159
        QSTAR=1.0
        IF(IS.EQ.1.AND.ISCODE(J).EQ.3)RETURN
        IF(IC.EQ.1.AND.ISCODE(J).EQ.2)RETURN
        IF(IC.EQ.1.AND.ISCODE(J).EQ.3)RETURN
        IF(ISCODE(J).EQ.4)RETURN
        TT=T
        A=AA(I)
        SIGMA=SSIG(I)-A
        EPS=EEPS(I)
C       WRITE(06,1031)SIGMA,EPS,A
 1031     FORMAT(5X,3E15.5)
C     ***CHECK FOR WHICH STRUCTURE IS FORMED***
        IF(IS.EQ.2) GO TO 6
C     ***CHECK FOR WHICH CAVITY IS OCCUPIED****
        IF(IC.EQ.2) GO TO 5
        RR=3.875
        Z=20.
        RR2=6.593
        Z2=20.0
        RR3=8.056
        Z3=50.0
        GO TO 8
C     ***STRUCTURE I CAVITY II
  5     RR=4.152
        Z=21.
        RR2=7.078
        Z2=24.0
        RR3=8.285
        Z3=50.0
        GO TO 8
  6     CONTINUE
C     ***CHECK FOR CAVITY, STRUCTURE II***
        IF(IC.EQ.2) GO TO 7
```

```
C     ***STRUCTURE II, CAVITY I***
        RR=3.87
        Z=20.
        RR2=6.667
        Z2=20.0
        RR3=8.079
        Z3=50.0
        GO TO 8
C     ***STRUCTURE II, CAVITY II***
 7      RR=4.703
        Z=28.
        RR2=7.464
        Z2=28.0
        RR3=8.782
        Z3=50.0
 8       CONTINUE
C
C       EVALUATE THE INTEGRAL AND RETURN THE VALUE OF C
        CALL YLIMIT(B)
        C=GAUSS(0.,B,10,OMEGA)
        PI=3.14159
        CC=C*4.*PI/T/1.38/9.869/10.
C       QSTAR CORRELATIONS.
        FORM=(SIGMA*OM(I)/(RR-A))*(EPS/273.15)
        IF(IS.EQ.1.AND.IC.EQ.1)QSTAR=DEXP(-35.3446*(FORM**0.973))
        IF(IS.EQ.1.AND.IC.EQ.2)QSTAR=DEXP(-14.1161*(FORM**0.8266))
        IF(IS.EQ.2.AND.IC.EQ.1)QSTAR=DEXP(-35.3446*(FORM**0.973))
        IF(IS.EQ.2.AND.IC.EQ.2)QSTAR=DEXP(-782.8469*(FORM**2.3129))
        CC=CC*QSTAR
C       WRITE(6,552)(FORM,QSTAR)
C552      FORMAT(1X,1F,2X,1F)
        RETURN
        END
C
C
C
C       ************************************************
        SUBROUTINE CUBEQN(A,Z,MTYPE)
C       ************************************************
C
C       THIS SUBROUTINE FINDS THE THREE ROOTS OF THE CUBIC
C       EQUATION GENERATED BY THE EQUATION OF STATE.
C
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
       DIMENSION A(4),Z(3),B(3)
       B(1)=A(2)/A(1)
       B10V3=B(1)/3.0
       B(2)=A(3)/A(1)
       B(3)=A(4)/A(1)
       ALF=B(2)-B(1)*B10V3
       BET=2.*B10V3**3-B(2)*B10V3+B(3)
       BETOV2=BET/2.
       ALFOV3=ALF/3.
       CUAOV3=ALFOV3**3
       SQBOV2=BETOV2**2
       DEL=SQBOV2+CUAOV3
```

```
      IF(DEL) 40,20,30
   20  MTYPE=0
       GAM=DSQRT(-ALFOV3)
      IF(BET) 22,22,21
   21  Z(1)=-2.*GAM-B10V3
       Z(2)=GAM-B10V3
       Z(3)=Z(2)
       GO TO 50
   22  Z(1)=2.*GAM-B10V3
       Z(2)=-GAM-B10V3
       Z(3)=Z(2)
      GO TO 50
   30 MTYPE=1
       EPS=DSQRT(DEL)
       TAU=-BETOV2
       RCU=TAU+EPS
       SCU=TAU-EPS
       SIR=1.
       SIS=1.
       IF(RCU) 31,32,32
   31  SIR=-1.
   32  IF(SCU) 33,34,34
   33 SIS=-1.
  34  R=SIR*(SIR*RCU)**.333333
      S=SIS*(SIS*SCU)**.333333
       Z(1)=R+S-B10V3
       Z(2)=-(R+S)/2.-B10V3
      Z(3)=0.866025*(R-S)
       GO TO 50
   40  MTYPE=-1
       QUOT=SQBOV2/CUAOV3
       ROOT=DSQRT(-QUOT)
       IF(BET) 42,41,41
   41 PEI=(1.570796+DATAN(ROOT/DSQRT(1.-ROOT**2)))/3.
       GO TO 43
   42  PEI=DATAN(DSQRT(1.-ROOT**2)/ROOT)/3.
   43  FACT=2.*DSQRT(-ALFOV3)
       Z(1)= FACT*DCOS(PEI)-B10V3
       Z(2)= FACT*DCOS(PEI+2.094395)-B10V3
       Z(3)=FACT*DCOS(PEI+4.188790)-B10V3
   50  RETURN
       END
C
C
C
C      ************************************************
       SUBROUTINE DATA(Y,XA,T)
C      ************************************************
C
C      THIS SUBROUTINE READS THERMODYNAMIC DATA FOR THE GASES,
C      CALCULATES MIXTURE CRITICAL PROPERITES, FREEZING POINT
C      DEPRESSIONS, AND ACTIVITY COEFFICIENTS FOR WATER IN
C      THE PRESENCE OF INHIBITORS.
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
       DIMENSION A(10),SIGMA(10),EPS(10)
       DIMENSION NCODE(10),KK(10)
```

```
      DIMENSION ZAA(1,25),AA(10,25)
      DIMENSION IISCO(25)
      DIMENSION Y(25),XA(25),ZA(20)
      DIMENSION X(11),TCIJ(10,10),ZC(10,10),PCIJ(10,10),VCIJ(10,10),
     2  PC(10),TC(10),VC(10),OMEGA(10),ESTAR(10),C1RKV(10),C2RKV(10),
     3  C1RKL(10),C2RKL(10),AMW(10),C0FREF(10),C1FREF(10),
     4  C2FREF(10),C3FREF(10),C4FREF(10),TS(10,10),
     5  AK(25,25),DVR(25,25),DTR(25,25)
      COMMON /PVTIJ/ OMEGA, PCIJ, TCIJ
      COMMON /AMOL/MA,ISCODE(10)
      COMMON /AZ/KK,N,MK
      COMMON /COEFF/ C0FREF, C1FREF, C2FREF, C3FREF, C4FREF,
     2       C0HNRY, C1HNRY, C2HNRY, C3HNRY, C4HNRY, C5HNRY,
     3       C0ALFS, C1ALFS, C2ALFS, C3ALFS, C4ALFS, C5ALFS
      COMMON /PVT/ RT, TC, PC, VC,  NSOLV
      COMMON/NC/NCODE,NCOMP
      COMMON /ACTVTY/ TS, ESTAR
      COMMON /VOL/   DVR, DTR, C1RKL, C2RKL
      COMMON /PHMX/ C1RKV, C2RKV
      COMMON/AFACT/OM(10)
      COMMON/FUND/SIGMA,EPS,A
      COMMON/BKSA/AK
      COMMON/BKSC/IWATER,IPOS,ISTR
      COMMON/IMP/IMPURE,IMCODE,XIMP(100),YCO2(100)
      COMMON/SOLUT/XSOLU,ACTIV,YYYCO2
      COMMON/TFREEZ/TT0
      COMMON/AWAT/ANN(25,25)
      IF(IWATER.EQ.0)GO TO 508
      MA=MA+1
      KK(MA)=13
508   CONTINUE
       DATA X1OLD/1./
      OPEN(10,FILE='TAPE10.DAT',STATUS='OLD')
      I=1
      DO 96 I2=1,25
      IF(IWATER.EQ.0)GO TO 51
      IF(I2.NE.13)GO TO 51
     READ(10,306)A(MA)     ,SIGMA(MA) ,EPS(MA)  ,AMW(MA)   ,TC(MA)
     READ(10,306)VC(MA)    ,   PC(MA) ,OMEGA(MA),ESTAR(MA) ,C1RKV(MA)
     READ(10,306)C2RKV(MA) ,C1RKL(MA) ,C2RKL(MA),C0FREF(MA),C1FREF(MA)
     READ(10,306)C2FREF(MA),C3FREF(MA),C4FREF(MA)
      READ(10,307)(AK(MA,J),J= 1, 6)
      READ(10,307)(AK(MA,J),J= 7,12)
      READ(10,307)(AK(MA,J),J=13,18)
      READ(10,307)(AK(MA,J),J=19,24)
      READ(10,307)(AK(MA,J),J=25,25)
      OM(MA)=OMEGA(MA)
      READ(10,308)ISCODE(MA)
      GO TO 96
51    IF(I2.EQ.KK(I)) GO TO 95
      READ(10,306)(ZA(J), J= 1, 5)
      READ(10,306)(ZA(J), J= 6,10)
      READ(10,306)(ZA(J), J=11,15)
      READ(10,306)(ZA(J), J=16,20)
      READ(10,307)(ZAA(1,J),J= 1, 6)
      READ(10,307)(ZAA(1,J),J= 7,12)
      READ(10,307)(ZAA(1,J),J=13,18)
```

```
        READ(10,307)(ZAA(1,J),J=19,24)
        READ(10,307)(ZAA(1,J),J=25,25)
        READ(10,308) IISCO(I)
        GO TO 96
 95     READ(10,306) A(I),SIGMA(I),EPS(I),AMW(I), TC(I)
        READ(10,306) VC(I),PC(I),OMEGA(I),ESTAR(I),C1RKV(I)
        READ(10,306) C2RKV(I),C1RKL(I),C2RKL(I),C0FREF(I),C1FREF(I)
        READ(10,306) C2FREF(I),C3FREF(I),C4FREF(I)
        READ(10,307)(AK(I,J),J= 1, 6)
        READ(10,307)(AK(I,J),J= 7,12)
        READ(10,307)(AK(I,J),J=13,18)
        READ(10,307)(AK(I,J),J=19,24)
        READ(10,307)(AK(I,J),J=25,25)
        OM(I)=OMEGA(I)
        READ(10,308) ISCODE(I)
        I=I+1
  96    CONTINUE
        REWIND(UNIT=10)
        CLOSE(UNIT=10)
C 306   FORMAT(10X,5(2X,E12.5),/,10X,5(2X,E12.5),/,10X,5(2X,E12.5),/
C    1 ,10X,5(2X,E12.5))
C 307   FORMAT(10X,6(2X,E12.5),/,10X,6(2X,E12.5),/,10X,6(2X,E12.5),/,
C    1  10X,6(2X,E12.5),/,12X,E12.5)
  306   FORMAT(5(E12.5,1X))
  307   FORMAT(6(E12.5,1X))
  308   FORMAT(I2)
        K=1
        DO 106 I=1,MA
        DO 107 J=1,25
        IF(J.NE.KK(K+1)) GO TO 107
        AA(I,K+1)=AK(I,J)
        K=K+1
  107   CONTINUE
        K=I+1
  106   CONTINUE
        DO 108 I=1,MA
        DO 109 J=1,MA
        AK(I,J)=0.0
        AK(I,J)=AA(I,J)
  109   CONTINUE
  108   CONTINUE
      DO 6 I=1,MA
      DO 6 J=1,MA
        AK(J,I)=AK(I,J)
      DVR(I,J)=DVR(J,I)
      DTR(I,J)=DTR(J,I)
      TS(I,J)=TS(J,I)
 6     CONTINUE
      RT=10.73*T
      J=0
        JJ=1
      DO 10 I=1,MA
        IF(IWATER.NE.0)GO TO 826
      IF(Y(I).LT.1.E-5) GO TO 10
 826    J=J+1
        JJ=JJ+1
      NCODE(J)=I
```

```
      XA(J)=Y(I)
      NCOMP=J
   10 CONTINUE
      DO 20 I=1,NCOMP
      EPS(I)=EPS(NCODE(I))
      SIGMA(I)=SIGMA(NCODE(I))
      A(I)=A(NCODE(I))
      ISCODE(I)=ISCODE(NCODE(I))
      OM(I)=OM(NCODE(I))
      PC(I)=PC(NCODE(I))
      TC(I)=TC(NCODE(I))
      VC(I)=VC(NCODE(I))
      OMEGA(I)=OMEGA(NCODE(I))
      ESTAR(I)=ESTAR(NCODE(I))
      C1RKV(I)=C1RKV(NCODE(I))
      C2RKV(I)=C2RKV(NCODE(I))
      C1RKL(I)=C1RKL(NCODE(I))
      C2RKL(I)=C2RKL(NCODE(I))
      C0FREF(I)=C0FREF(NCODE(I))
      C1FREF(I)=C1FREF(NCODE(I))
      C2FREF(I)=C2FREF(NCODE(I))
      C3FREF(I)=C3FREF(NCODE(I))
      C4FREF(I)=C4FREF(NCODE(I))
      TCIJ(I,I) = TC(NCODE(I))
      AMW(I)=AMW(NCODE(I))
   20 CONTINUE
      IF(NCOMP.EQ.1) GO TO 22
C       IF(IWATER.NE.0.AND.(NCOMP-1).EQ.1)GO TO 22
      NCOMP1=NCOMP-1
      DO 21 I=1,NCOMP1
      I1=I+1
      DO 21 J=I1,NCOMP
      TS(I,J)=TS(NCODE(I),NCODE(J))
      TS(J,I)=TS(I,J)
      DVR(I,J)=DVR(NCODE(I),NCODE(J))
      DVR(J,I)=DVR(I,J)
      DTR(I,J)=DTR(NCODE(I),NCODE(J))
      DTR(J,I)=DTR(I,J)
      AK(I,J) = AK(NCODE(I),NCODE(J))
       ZC(I,J)=.291-.04*(OMEGA(I)+OMEGA(J))
      ZC(J,I)=ZC(I,J)
       TCIJ(I,J)=(TC(I)*TC(J))**.5*(1.-AK(I,J))
      TCIJ(J,I)=TCIJ(I,J)
      VCIJ(I,J)=(.5*(VC(I)**.3333333+VC(J)**.333333))**3
      VCIJ(J,I)=VCIJ(I,J)
      PCIJ(I,J)=ZC(I,J)*10.73*TCIJ(I,J)/VCIJ(I,J)
      PCIJ(J,I)=PCIJ(I,J)
   21  CONTINUE
 22    CONTINUE
        DO 31 I3=1,NCOMP
        DO 31 I4=1,NCOMP
        ANN(I3,I4)=AK(I3,I4)
 31     CONTINUE
        IF(IWATER.EQ.0)GO TO 507
        MA=MA-1
        NCOMP=NCOMP-1
        ACTIV=1.0
```

```
        TT0=0.0
 507    IF(IMPURE.EQ.0.OR.XSOLU.EQ.0.0)GO TO 509
        T=T/1.8
C
C    ** ACTIVITY COEFFICIENT OF WATER **
C
        IF(IMCODE.EQ.1)ACTIV=DEXP(-0.90634*XSOLU**2+1.95522*XSOLU**3)
        IF(IMCODE.EQ.2)ACTIV=DEXP(5.77435*XSOLU**2)
        IF(IMCODE.EQ.3)ACTIV=DEXP(-0.90634*XSOLU**2+1.95522*XSOLU**3)
        IF(IMCODE.EQ.4)ACTIV=DEXP(-0.29965*XSOLU**2-172.56293*XSOLU**3)
        IF(IMCODE.EQ.5)ACTIV=DEXP(-199.63879*XSOLU**2+3869.86893*XSOLU
     1                 **3)
        IF(IMCODE.EQ.6)ACTIV=DEXP(-239.55098*XSOLU**2+9683.44617*XSOLU
     1                 **3)
        IF(IMCODE.EQ.7)ACTIV=DEXP(((10.44*T-3535.34)*XSOLU**2.+
     1                 (-32.19*T+10888.7)*XSOLU**3.)/(0.082*T))
        IF(IMCODE.EQ.8)ACTIV=DEXP(-1.84825*XSOLU**2+4.26904*XSOLU**3)
        IF(IMCODE.EQ.9.OR.IMCODE.EQ.10)ACTIV=DEXP(((-64.2019)
     1*XSOLU**2.+(183.219)*XSOLU**3.)/(0.082*T))
C
C   ** CORRECTION FACTOR FOR SYSTEMS CONTAINING CO2 **
C
        ACTIV=(1-0.30*YYYCO2*XSOLU)*ACTIV
C
C   ** FREEZING POINT DEPRESSIONS **
C
        IF(IMCODE.EQ.1)TT0=-0.13171+105.59*XSOLU+161.82*XSOLU**2
     1  -70.233*XSOLU**3
        IF (IMCODE.EQ.2)TT0=-0.33398+109.91*XSOLU+308.25*XSOLU**2
     1 -745.82*XSOLU**3
        IF(IMCODE.EQ.3)TT0=-1.1132+161.707*XSOLU-101.0468*XSOLU**2.
        IF(IMCODE.EQ.4)TT0=-0.083176+197.62*XSOLU-175.14*XSOLU**2
     1  +8884.6*XSOLU**3
        IF(IMCODE.EQ.5)TT0=0.12618+207.67*XSOLU+6510.4*XSOLU**2
     1  +4113.4*XSOLU**3
        IF(IMCODE.EQ.6)TT0=0.0085870+185.53*XSOLU-65.062*XSOLU**2
     1  +494.73*XSOLU**3
        IF(IMCODE.EQ.7)TT0=0.0460878+163.998*XSOLU+941.4078*XSOLU**2.
        IF(IMCODE.EQ.8)TT0=-0.019306+104.71*XSOLU+64.867*XSOLU**2
     1  +1857.6*XSOLU**3
        IF(IMCODE.EQ.9.OR.IMCODE.EQ.10)TT0=-0.11843+110.2595*XSOLU+
     1126.4329*XSOLU**2.
        T=T*1.8
 509    RETURN
      END
C
C
C       ****************************************************
        DOUBLE PRECISION FUNCTION DEL(N)
C       ****************************************************
C
C       THE DEL FUNCTIONS EVALUATE DEL OF THE KIHARA FUNCTION FOR
C       THE 1ST, 2ND AND 3RD SHELLS OF WATER.
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /SIG/ SIGMA,EPS,RR,Z,A,T,RR2,Z2,RR3,Z3
      COMMON /RRR/ R
```

```
      D=(1.-R/RR-A/RR)
      DD=(1.+R/RR-A/RR)
      D=1.0/D**N - 1.0/DD**N
      DEL=  D/N
 2000 FORMAT('   DEL;   ', 1G10.5)
      RETURN
      END
C
C
C
C       ******************************************************
        DOUBLE PRECISION FUNCTION DEL2(N)
C       ******************************************************
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        COMMON/SIG/SIGMA,EPS,RR,Z,A,T,RR2,Z2,RR3,Z3
        COMMON/RRR/R
        D=(1.0-R/RR2-A/RR2)
        DD=(1.0+R/RR2-A/RR2)
        D=1.0/D**N-1.0/DD**N
        DEL2=D/N
        RETURN
        END
C
C
C
C       ******************************************************
        DOUBLE PRECISION FUNCTION DEL3(N)
C       ******************************************************
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        COMMON/SIG/SIGMA,EPS,RR,Z,A,T,RR2,Z2,RR3,Z3
        COMMON/RRR/R
        D=(1.0-R/RR3-A/RR3)
        DD=(1.0+R/RR3-A/RR3)
        D=1.0/D**N-1/DD**N
        DEL3=D/N
        RETURN
        END
C
C
C
C       ************************************************
        DOUBLE PRECISION FUNCTION GAUSS(A,B,M,FUNCTN)
C       ************************************************
C     ****REF: CARNAHAN,LUTHER AND WILKES:APP. NUMERICAL METH'S.
C     ****WILEY & SONS,INC.(1969).
C
C       FORMULA TO COMPUTE THE INTEGRAL OF FUNCTN(X) BETWEEN THE
C       INTEGRATION LIMITS A AND B.
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION NPOINT(7), KEY(8),Z(24),WEIGHT(24)
      EXTERNAL FUNCTN
C
C     **PRESET NPOINT,KEY,Z,AND WEIGHT ARRAYS
      DATA NPOINT /2,3,4,5,6,10,15/
      DATA KEY / 1,2,4,6,9,12,17,25 /
      WEIGHT(1)= 1.0
      WEIGHT(2)= 0.888888889
```

```
      WEIGHT(3)= 0.555555556
      WEIGHT(4)=0.652145155
      WEIGHT(5)=0.347854845
      WEIGHT(6)=0.568888889
      WEIGHT(7)= 0.478628671
      WEIGHT(8)= 0.236926885
      WEIGHT(9)= 0.467913935
      WEIGHT(10)= 0.360761573
      WEIGHT(11)= 0.171324493
      WEIGHT(12)= 0.295524225
      WEIGHT(13)= 0.269266719
      WEIGHT(14)= 0.219086363
      WEIGHT(15)= 0.149451349
      WEIGHT(16)= 0.066671344
      WEIGHT(17)= 0.202578242
      WEIGHT(18)= 0.198431485
      WEIGHT(19)= 0.186160000
      WEIGHT(20)= 0.166269206
      WEIGHT(21)= 0.139570678
      WEIGHT(22)= 0.107159221
      WEIGHT(23)= 0.070366047
      WEIGHT(24)= 0.030753242
      Z(1)=0.577350269
      Z(2)=0.0
      Z(3)=0.774596669
      Z(4)=0.339981044
      Z(5)=0.861136312
      Z(6)=0.0
      Z(7)=0.538469310
      Z(8)=0.906179846
      Z(9)=0.238619186
      Z(10)=0.661209387
      Z(11)=0.932469514
      Z(12)=0.148874339
      Z(13)=0.433395394
      Z(14)=0.679409568
      Z(15)=0.865063367
      Z(16)= 0.973906529
      Z(17)= 0.0
       Z(18)=0.2011941
       Z(19)=0.3941513
       Z(20)=0.5709722
       Z(21)=0.7244177
      Z(22)= 0.848206583
      Z(23)= 0.937273392
      Z(24)=0.987992518
C      *** FIND SUBSCRIPT OF FIRST Z AND WEIGHT VALUE ***
      DO 1 I=1,7
      IF(M.EQ.NPOINT(I)) GO TO 2
    1 CONTINUE
C     *** INVALID M USED ***
      GAUSS=0.
      RETURN
C
C     *** SET UP INITIAL PARAMETERS ***
    2 JFIRST=KEY(I)
      JLAST=KEY(I+1)-1
```

```
      C=(B-A)/2.
      D=(B+A)/2.
C
C     *** ACCUMULATE THE SUM IN THE MPOINT FORMULA
      SUM=0.
      DO 5 J=JFIRST,JLAST
      IF( Z(J).EQ.0.0 ) SUM=SUM+WEIGHT(J)*FUNCTN(D)
    5 IF( Z(J).NE.0.0 ) SUM=SUM+WEIGHT(J)*(FUNCTN(Z(J)*C+D)
     2 + FUNCTN( -Z(J)*C +D))
C
C     *** MAKE INTERVAL CORRECTION AND RETURN ****
      GAUSS=C*SUM
 2100 FORMAT('   GAUSS;    ',1G10.5)
      RETURN
      END
C
C
C
C       ********************************************
        DOUBLE PRECISION FUNCTION OMEGA(R)
C       ********************************************
C
C     THIS FUNCTION EVALUATES THE CELL POTENTIAL( SPHERICALLY
C     SYMETRIC KIHARA) WITH THE RADIAL POSITION, R, OF THE
C     MOLECULE IN THE CAVITY AS THE INDEPENDENT VARIABLE.
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /SIG/ SIGMA,EPS,RR,Z,A,T,RR2,Z2,RR3,Z3
      COMMON /RRR/ ZZ
      ZZ=R
      OMEGA=2.*Z*EPS*(SIGMA**12/RR**11/R*(DEL(10)+A/RR*DEL(11))
     1  - SIGMA**6/RR**5/R*(DEL(4)+A/RR*DEL(5)))
        OMEGA2=2.0*Z2*EPS*(SIGMA**12/RR2**11/R*(DEL2(10)+A/RR2*DEL2(11))
     1  -SIGMA**6/RR2**5/R*(DEL2(4)+A/RR2*DEL2(5)))
        OMEGA3=2.0*Z3*EPS*(SIGMA**12/RR3**11/R*(DEL3(10)+A/RR3*DEL3(11))
     1  -SIGMA**6/RR3**5/R*(DEL3(4)+A/RR3*DEL3(5)))
        OMEGA=OMEGA+OMEGA2+OMEGA3
      OMEGA=-OMEGA/T
      IF(ABS(OMEGA).GT. 170.) OMEGA=ABS(OMEGA)/OMEGA*170.
      IF (OMEGA.LE.-60.) OMEGA=-60.
      OMEGA=DEXP(OMEGA)*R*R
 2300 FORMAT('   OMEGA;   ', 1G10.5)
      RETURN
      END
C
C
C       ************************************************
        SUBROUTINE VAPRES(PVAP,T)
C       ************************************************
C
C       THIS SUBROUTINE IS CALLED BY BUBDEW. IT CALCULATES THE VAPOR PRESSURE
C       OF EACH COMPONENT USING RIEDEL'S CORRELATION.
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        DIMENSION PVAP(10)
        DIMENSION TCIJ(10,10),PCIJ(10,10),PC(10),TC(10),VC(10),OMEGA(10)
        DIMENSION NCODE(10)
```

```
      COMMON/PVTIJ/OMEGA,PCIJ,TCIJ
      COMMON/NC/NCODE,NCOMP
      COMMON/PVT/RT,TC,PC,VC,NSOLV
      DO 401 I=1,NCOMP
      TR=T/TC(I)
      IF(TR.GT.1.0)GO TO 400
      B=36./TR-35.-TR**6.0+42.*DLOG(TR)
      ALFAC=5.808+4.93*OMEGA(I)
      RES=0.118*B-7*DLOG10(TR)+(ALFAC-7.)*(0.036*B-DLOG10(TR))
      PVAP(I)=PC(I)/10.**(RES)
      GO TO 401
 400  PVAP(I)=PC(I)
 401  CONTINUE
      RETURN
      END
C
C     *******************************************************
      SUBROUTINE BUBDEW(T,P,Y)
C     *******************************************************
C
C     THIS SUBROUTINE CALCULATES THE DEW POINT PRESSURE IF LIQ=0 AND
C     BUBBLE POINT PRESSURE IF LIQ=1
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION XL(10),Y(10),V(10),PHIL(10)
      DIMENSION PHI(10),PVAP(10)
      DIMENSION NCODE(10)
      DIMENSION ZK(10),ZCN(10)
      COMMON/X/XL
      COMMON/PH/PHIL
      COMMON/NC/NCODE,NCOMP
      COMMON/TBLOC/ITAG
      COMMON/LIQUID/LIQ
      COMMON/HELP/IST0,IST2,ISLOW
C
C
      ITAG=1
      ITER=0
      CALL VAPRES(PVAP,T)
      SFRAC=0
      IF(LIQ.EQ.1)GO TO 8000
C ** DEW POINT CALCULATIONS **
      DO 280 I=1,NCOMP
      FRAC=Y(I)/PVAP(I)
      SFRAC=SFRAC+FRAC
 280  CONTINUE
C     MAKE AN INITIAL ESTIMATE OF PRESSURE
      P=1/SFRAC
 288  S=0
      DO 201 I=1,NCOMP
      XL(I)=Y(I)*P/PVAP(I)
      S=S+XL(I)
 201  CONTINUE
      DO 222 I=1,NCOMP
      XL(I)=XL(I)/S
 222  CONTINUE
 206  CALL PHIMIX(Y,P,T,PHI)
```

```
        SUM=0.0
        DO 202 I=1,NCOMP
        ZK(I)=PHIL(I)/PHI(I)
        ZCN(I)=Y(I)/ZK(I)
        SUM=SUM+ZCN(I)
 202    CONTINUE
        DO 203 I=1,NCOMP
        XL(I)=ZCN(I)/SUM
 203    CONTINUE
        PNEW=P/SUM
        IF(ABS(SUM-1.0).LT.0.0001)GO TO 205
        P=PNEW
        ITER=ITER+1
        IF(ITER.GT.100)GO TO 207
        GO TO 206
 207    WRITE(6,208)
 208    FORMAT(' FAILED TO CONVERGE IN BUBDEW')
        GO TO 205
C ** BUBBLE POINT CALCULATIONS **
C   HERE XL IS SET EQUAL TO Y BECAUSE THE VALUES OF Y COMING IN
C       ARE LIQUID COMPOSITION
 8000                   DO 101 I=1,NCOMP
        XL(I)=Y(I)
 101    CONTINUE
        DO 102 I=1,NCOMP
        FRAC=XL(I)*PVAP(I)
        SFRAC=FRAC+SFRAC
 102    CONTINUE
C       MAKE AN INITIAL ESTIMATE OF PRESSURE
        P=SFRAC
        S=0
        DO 103 I=1,NCOMP
        Y(I)=XL(I)*PVAP(I)/P
        S=S+Y(I)
 103    CONTINUE
        DO 104 I=1,NCOMP
        Y(I)=Y(I)/S
 104    CONTINUE
 105    CALL PHIMIX(Y,P,T,PHI)
        SUM=0.0
        DO 106 I=1,NCOMP
        ZK(I)=PHIL(I)/PHI(I)
        ZCN(I)=ZK(I)*XL(I)
        SUM=SUM+ZCN(I)
 106    CONTINUE
        DO 107 I=1,NCOMP
        Y(I)=ZCN(I)/SUM
 107    CONTINUE
        PNEW=P*SUM
        IF(ABS(SUM-1.0).LT.0.0001)GO TO 225
        P=PNEW
        ITER=ITER+1
        IF(ITER.GT.100)GO TO 207
        GO TO 105
C       INTERCHANGE XL AND Y VALUES AGAIN BY STORING Y VALUES IN V
 225    DO 23 I=1,NCOMP
        V(I)=Y(I)
```

```
        Y(I)=XL(I)
        XL(I)=V(I)
 23     CONTINUE
 205            RETURN
        END
C
C
C       ************************************************
         SUBROUTINE PHIMIX(Y,P,T,PHI)
C       ************************************************
C
C
C
C       ** THIS SUBROUTINE IS TAKEN DIRECTLY FROM PRAUSNITZ
C           AND CHUEH'S BOOK "COMPUTER CALCULATIONS FOR MULTI
C           COMPONENT VAPOR LIQUID EQUILIBRIA"(1968) PRENTICE HALL
C
C       THIS SUBROUTINE CALCULATES THE FUGACITY COEFFICIENTS FOR
C       EACH COMPONENT FROM THE EQUATION OF STATE.
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION NCODE(10)
      DIMENSION X(11),TCIJ(10,10),ZC(10,10),PCIJ(10,10),VCIJ(10,10),
     2 PC(10),TC(10),VC(10),OMEGA(10),ESTAR(10),C1RKV(10),C2RKV(10),
     3 C1RKL(10),C2RKL(10),AMW(10),C0FREF(10),C1FREF(10),
     4 C2FREF(10),C3FREF(10),C4FREF(10),TS(10,10),
     5 AK(25,25),DVR(25,25),DTR(25,25)
        DIMENSION PHIL(10)
        DIMENSION XL(10)
      COMMON/BLOCK/ISOLVE
      COMMON /PHMX/ C1RKV, C2RKV
      COMMON /PVTIJ/ OMEGA, PCIJ, TCIJ
      COMMON /PVT/ RT, TC, PC, VC,  NSOLV
      COMMON/NC/NCODE,NCOMP
      COMMON/AFACT/OM(10)
      COMMON/BKSA/AK
        COMMON/X/XL
        COMMON/PHAS/NVLLH
        COMMON/PH/PHIL
        COMMON/TBLOC/ITAG
        COMMON/ZV/ZV
        COMMON/WATER/NW
        COMMON/AWAT/ANN(25,25)
        COMMON/CRITCL/NCRIT,TCRIT
        COMMON/LIQUID/LIQ
      DIMENSION Y(10),PHI(10),Z(3),ARKV(10,10),
     2BRKV(10),AIRKV(10),A(4),AMWT(10,10)
      DIMENSION AA(25),BTC(25),AY(25,25)
       IF(ISOLVE.EQ.1)GO TO 200
       DO 100 I=1,NCOMP
       ARKV(I,I)=C1RKV(I)*10.73**2*TC(I)**2.5/PC(I)
       BRKV(I)=C2RKV(I)*10.73*TC(I)/PC(I)
       IF(I.EQ.NCOMP) GO TO 110
       I1=I+1
       DO 100 J=I1,NCOMP
      ARKV(I,J)=(C1RKV(I)+C1RKV(J))*0.5*10.73**2*TCIJ(I,J)
     1**2.5/PCIJ(I,J)
       ARKV(J,I)=ARKV(I,J)
```

```
  100  CONTINUE
  110  CONTINUE
       AMRKV=0.
       BMRKV=0.
       DO 120 I=1,NCOMP
       AIRKV(I)=0.
       BMRKV=BMRKV+Y(I)*BRKV(I)
       DO 120 J=1,NCOMP
       AIRKV(I)=AIRKV(I)+Y(J)*ARKV(I,J)
  120  AMRKV=AMRKV+Y(I)*Y(J)*ARKV(I,J)
C
C          CALCULATE VAPOR MOLAR VOLUME FOR MIXTURE
C
       A(1)=1.
       A(2)=-1.
       PBRT=P*BMRKV/RT
       ABRT=AMRKV/(BMRKV*10.72999*T**1.5)
       A(3)=PBRT*(ABRT-1.-PBRT)
       A(4)=-ABRT*(PBRT**2)
       CALL CUBEQN(A,Z,MTYPE)
       IF(MTYPE)130,140,140
  130  AMAX1=Z(1)
       IF(AMAX1.LT.Z(2)) AMAX1=Z(2)
       IF(AMAX1.LT.Z(3)) AMAX1=Z(3)
       ZV=AMAX1
       GO TO 150
  140  ZV=Z(1)
  150  VV=ZV*RT/P
C
C            CALCULATE FUGACITY COEFFICIENTS WITH THE
C            MODIFIED REDLICH-KWONG EQUATION OF STATE
C
      QVVB=DLOG(VV/(VV-BMRKV))
      Q1VB=1./(VV-BMRKV)
       Q2RTB=2./(10.73*T**1.5*BMRKV)
       QVBV=DLOG((VV+BMRKV)/VV)
       QARTB=AMRKV/(10.73*T**1.5*BMRKV**2)
       QBVB=BMRKV/(VV+BMRKV)
        DO 160 I=1,NCOMP
      PHI(I)=QVVB+BRKV(I)*Q1VB-AIRKV(I)*Q2RTB*QVBV+
     2 BRKV(I)*QARTB*(QVBV-QBVB)-DLOG(ZV)
      IF(PHI(I).LT.170.0) GO TO 27
      WRITE(6,28) QVVB,BRKV(I),Q1VB,AIRKV(I),Q2RTB,QVBV,
     2 QARTB,QBVB,ZV
 28    FORMAT(9F10.5)
 27      CONTINUE
      PHI(I)=DEXP(PHI(I))
 160     CONTINUE
       RETURN
C
C      ****** CALCULATE FUGACITY COEFFICIENTS USING PENG ******
C      ****** ROBINSON EQUATION OF STATE                 ******
C
  200  BC=0.0
       BCX=0.0
       DO 201 I=1,NCOMP
       AKK=0.37464+1.54226*OMEGA(I)-0.26992*OMEGA(I)**2
```

```
      ATC=52.643367*TC(I)**2/PC(I)
       IF(NW.EQ.0)GO TO 211
       DO 81 I1=1,NCOMP
       AK(I1,NCOMP)=ANN(I1,NCOMP)*(0.4605*P/T-0.2237)
       AK(NCOMP,I1)=AK(I1,NCOMP)
81     CONTINUE
       IF(I.LT.NCOMP)GO TO 211
       IF((T/TC(I)).LT.0.85)ALPHA=(1.0085677+0.82154*(1.-DSQRT(T/TC(I)
    1)))**0.5
       IF((T/TC(I)).GE.0.85)GO TO 211
       GO TO 212
211       ALPHA=(1.0+AKK*(1.0-DSQRT(T/TC(I))))**2
212      AA(I)=ATC*ALPHA
      BTC(I)=0.834794*TC(I)/PC(I)
      BC=BC+Y(I)*BTC(I)
       BCX=BCX+XL(I)*BTC(I)
 201  CONTINUE
      AC=0.0
       ACX=0.0
      DO 202 I=1,NCOMP
      DO 203 J=1,NCOMP
      AY(I,J)=(1.0-AK(I,J))*DSQRT(AA(I)*AA(J))
      AC=AC+Y(I)*Y(J)*AY(I,J)
       ACX=ACX+XL(I)*XL(J)*AY(I,J)
 203  CONTINUE
 202  CONTINUE
       NCRIT=0
       IF(LIQ.EQ.1)GO TO 809
       IF(NVLLH.EQ.0)GO TO 809
       TCRIT=(AC/BC)/63.061506
       IF((T/TCRIT).GT.0.97)GO TO 808
       GO TO 809
808    NCRIT=1
       GO TO 810
809    CONTINUE
       IF(ITAG.EQ.2)GO TO 288
      AP=AC*P/(10.73*T)**2
      B=BC*P/(10.73*T)
      A(1)=1
      A(2)=B-1
      A(3)=AP-3.0*B**2-2.0*B
      A(4)=B**3+B**2-AP*B
      CALL CUBEQN(A,Z,MTYPE)
      IF(MTYPE)204,205,205
 204  AMAX1=Z(1)
      IF(AMAX1.LT.Z(2))AMAX1=Z(2)
      IF(AMAX1.LT.Z(3))AMAX1=Z(3)
      ZV=AMAX1
      GO TO 206
 205  ZV=Z(1)
 206  DO 207 I=1,NCOMP
      F1=BTC(I)/BC*(ZV-1.0)
      F2=-DLOG(ZV-B)
      F3=0.0
      DO 208 K=1,NCOMP
      F3=F3+Y(K)*AY(K,I)
 208  CONTINUE
```

```
       F3=-AP/(2.828427*B)*(2.0*F3/AC-BTC(I)/BC)
       F3=F3*DLOG((ZV+2.414*B)/(ZV-0.414*B))
       PHI(I)=DEXP(F1+F2+F3)
  207  CONTINUE
        IF(NVLLH.EQ.0.OR.ITAG.EQ.0)GO TO 810
 288    APX=ACX*P/(10.73*T)**2.
        BX=BCX*P/(10.73*T)
        A(1)=1
        A(2)=BX-1
        A(3)=APX-3.0*BX**2.-2.*BX
        A(4)=BX**3.+BX**2.-APX*BX
        CALL CUBEQN(A,Z,MTYPE)
        IF(MTYPE)214,215,216
 214    AMINI=Z(1)
        IF(AMINI.GT.Z(2).AND.Z(2).GT.0)AMINI=Z(2)
        IF(AMINI.GT.Z(3).AND.Z(3).GT.0)AMINI=Z(3)
        ZL=AMINI
        GO TO 217
 215    ZL=Z(2)
        GO TO 217
 216    ZL=Z(1)
 217    DO 218 I=1,NCOMP
        F1=BTC(I)/BCX*(ZL-1.0)
        F2=-DLOG(ZL-BX)
        F3=0.0
        DO 219 K=1,NCOMP
        F3=F3+XL(K)*AY(K,I)
 219    CONTINUE
        F3=-APX/(2.828427*BX)*(2.0*F3/ACX-BTC(I)/BCX)
        F3=F3*DLOG((ZL+2.414*BX)/(ZL-0.414*BX))
        PHIL(I)=DEXP(F1+F2+F3)
 218    CONTINUE
 810    RETURN
C
       END
C
C
C
C       ***********************************************
        SUBROUTINE YLIMIT(RLIMIT)
C       ***********************************************
C
C     ..... COPIED FROM W. R. PARRISH'S THESIS(BERKLEY)
C
C       THIS SUBROUTINE CALCULATES THE UPPER LIMIT OF
C       INTEGRATION IN THE SMOOTH CELL LANGMUIR CONSTANT
C       EXPRESSION.
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /SIG/ SIGMA,EPS,RR,Z,A,T,RR2,Z2,RR3,Z3
      CA=A/RR
      CHECK=0.0
      RCA=SIGMA/RR*1.122462
      S=1-0.98*(SIGMA/(2*(RR-A)))
      IF(S.LT.0.4) S=0.4
      RCA6=RCA**6
      RCA12=RCA**12
```

```
      DO 2 N=1,20
      IF( S.GT.1..OR.S.LE.0.) GO TO 6
      UM=1./(1.-S-CA)
      UP=1./(1.+S-CA)
      UM5=UM**5
      UP5=UP**5
      DA4=UM5+UP5
      DA5=UM5*UM+UP5*UP
      DB6=DA4+CA*DA5
      UM11=UM**11
      UP11=UP**11
      DA10=UM11+UP11
      DA11=UM11*UM+UP11*UP
      DB12=DA10+CA*DA11
      DB=RCA12*DB12-2.*RCA6*DB6
      A10=UM11/UM-UP11/UP
      A11=UM11-UP11
      B12=A10/10. + CA*A11/11
      A4=UM5/UM-UP5/UP
      A5=UM5-UP5
      B6=A4/4.+CA*A5/5.
      B=RCA12*B12-2.*RCA6*B6
      W=Z*EPS/(2.*S*T)*B
      DWY=-W/S+Z*EPS*DB/(2.*S*T)
      DS=S-(W-10.)/DWY
      IF(ABS((DS-S)/DS).LT..01) GO TO 3
      IF(DS.LE.0) CHECK=CHECK+1
      IF(DS.LE.0) DS=S*1.05
      IF(CHECK.GT.5) GO TO 6
    2 S=DS
    3 RLIMIT=S*RR
      RETURN
    6 CONTINUE
      WRITE(6,100)SIGMA,EPS,A,RR,Z,T,S
 100   FORMAT(' ','BLOW UP ON Y-LIMIT',7F10.5)
      RETURN
      END
C
C
C      ********************************************
C       REVISED SOLUBILITY SUBROUTINE
C
        SUBROUTINE SOL7(JK,Y7,PHI7,P,T,X6)
C      ********************************************
C
C       THIS SUBROUTINE CALCULATES THE SOLUBILITIES OF
C       THE GASES IN WATER USING KRICHEVSKY-KASARNOVSKY
C       EXPRESSIONS FOR EACH GAS.
C
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION A(25),B(25),C(25),D(25)
      DIMENSION VBAR(25),NCODE(25)
      COMMON/NC/NCODE,NCOMP
C
C     P IS IN ATM. AND T IS IN K
C
      DATA A/-15.826227,-18.400368,-18.057885,-20.958631,
```

```
     A       -67.557,-22.150557,-20.108263,0.0,0.0,0.0
     A       ,-868.764,0.0,0.0,-357.802,-14.283146,
     C       -17.160634,-17.934347,-15.103508,-17.979226,
     D       -336.76,-270.967,-877.845,-20.108263,
     E       -20.108263,0.0/
C
      DATA B/1559.0631,2410.4807,2627.6108,3109.3918,
     A       9177.534,3407.2181,2739.7313,0.0,0.0,0.0
     B       ,43323.6,0.0,0.0,13897.5,2050.3269,1915.144,
     C       1933.381,2603.9795,2530.0405,16170.1,
     D       15992.9,42051.0,2739.7313,2739.7313,0.0/
C
      DATA C/0.0,0.0,0.0,0.0,0.072775,
     A       0.0,0.0,0.0,0.0,0.0,
     B       122.986,0.0,0.0,52.2871,0.0,
     C       0.0,0.0,0.0,0.0,46.2117,
     D       33.2892,125.018,0.0,0.0,0.0/
C
      DATA D/1.0,1.0,1.0,1.0,760.0,
     A       1.0,1.0,1.0,1.0,1.0,
     B       0.0,1.0,0.0,-0.029836,1.0,
     C       1.0,1.0,1.0,1.0,-0.00608793,
     D       0.0260485,0.0,1.0,1.0,1.0/
C
      DATA VBAR/32.0,32.0,60.0,13*32.0,
     A          32.8,8*32.0/
C
C
      IF(JK.EQ.20.OR.JK.EQ.21.OR.JK.EQ.14.OR.JK.EQ.11.
     AOR.JK.EQ.22)GO TO 10
      IF(JK.EQ.8.OR.JK.EQ.9.OR.JK.EQ.10.OR.JK.EQ.12.
     AOR.JK.EQ.6.OR.JK.EQ.7)GO TO 20
      XO=D(JK)*DEXP(A(JK)+B(JK)/T+C(JK)*T)
      GO TO 30
  10  XO=DEXP((A(JK)+B(JK)/T+C(JK)*DLOG(T)+
     AD(JK)*T)/1.987)
  30  F=P*Y7*PHI7
      X6=F*XO*DEXP(-1.0*VBAR(JK)*(P-1.0)/(82.06*T))
      IF(X6.GT.0.05)GO TO 40
      GO TO 50
 40     CONTINUE
C     WRITE(6,200)JK,X6
      X6=0.05
      GO TO 50
C 20  WRITE(6,100)JK
 20       X6=0.0
 50     RETURN
 100  FORMAT(1X,T20,' * * COMPONENT# ',I3,' NOT YET
     A AVAILABLE IN SOL7 * * ')
 200  FORMAT(1X,T20,'* * COMPONENT# ',I3,' HAS DEFAULTED
     A TO X6 = 0.05 FROM X6 = ',E15.5,'  * * ')
C
      END
```

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BIBLIOGRAPHY

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